U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-254 387

Measurement of Atmospheric Sulfates: Literature Search & Methods Selection

Midwest Research Institute

Prepared For
Environmental Monitoring & Support Lab.

March 1976

KEEP UP TO DATE

Between the time you ordered this report—which is only one of the hundreds of thousands in the NTIS information collection available to you—and the time you are reading this message, several *new* reports relevant to your interests probably have entered the collection.

Subscribe to the **Weekly Government Abstracts** series that will bring you summaries of new reports *as soon as they are received by NTIS* from the originators of the research. The WGA's are an NTIS weekly newsletter service covering the most recent research findings in 25 areas of industrial, technological, and sociological interest—invaluable information for executives and professionals who must keep up to date.

The executive and professional information service provided by NTIS in the **Weekly Government Abstracts** newsletters will give you thorough and comprehensive coverage of government-conducted or sponsored research activities. And you'll get this important information within two weeks of the time it's released by originating agencies.

WGA newsletters are computer produced and electronically photocomposed to slash the time gap between the release of a report and its availability. You can learn about technical innovations immediately—and use them in the most meaningful and productive ways possible for your organization. Please request NTIS-PR-205/PCW for more information.

The weekly newsletter series will keep you current. But *learn what you have missed in the past* by ordering a computer **NTISearch** of all the research reports in your area of interest, dating as far back as 1964, if you wish. Please request NTIS-PR-186/PCN for more information.

WRITE: Managing Editor
5285 Port Royal Road
Springfield, VA 22161

Keep Up To Date With SRIM

SRIM (Selected Research in Microfiche) provides you with regular, automatic distribution of the complete texts of NTIS research reports *only* in the subject areas you select. SRIM covers almost all Government research reports by subject area and/or the originating Federal or local government agency. You may subscribe by any category or subcategory of our WGA **(Weekly Government Abstracts)** or **Government Reports Announcements and Index** categories, or to the reports issued by a particular agency such as the Department of Defense, Federal Energy Administration, or Environmental Protection Agency. Other options that will give you greater selectivity are available on request.

The cost of SRIM service is only 45¢ domestic (60¢ foreign) for each complete microfiched report. Your SRIM service begins as soon as your order is received and processed and you will receive biweekly shipments thereafter. If you wish, your service will be backdated to furnish you microfiche of reports issued earlier.

Because of contractual arrangements with several Special Technology Groups, not all NTIS reports are distributed in the SRIM program. You will receive a notice in your microfiche shipments identifying the exceptionally priced reports not available through SRIM.

A deposit account with NTIS is required before this service can be initiated. If you have specific questions concerning this service, please call (703) 451-1558, or write NTIS, attention SRIM Product Manager.

This information product distributed by

NTIS U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
5285 Port Royal Road
Springfield, Virginia 22161

PB 254 387

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ENVIRONMENTAL MONITORING series. This series describes research conducted to develop new or improved methods and instrumentation for the identification and quantification of environmental pollutants at the lowest conceivably significant concentrations. It also includes studies to determine the ambient concentrations of pollutants in the environment and/or the variance of pollutants as a function of time or meteorological factors.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

[redacted]

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO
EPA-600/4-76-008

2.

3. RECIPIENT'S ACCESSION NO.

4. TITLE AND SUBTITLE
MEASUREMENT OF ATMOSPHERIC SULFATES: LITERATURE SEARCH AND METHODS SELECTION

5. REPORT DATE
[redacted] 2, 1976 MARCH

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Fred J. Bergman

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Midwest Research Institute
425 Volker Boulevard
Kansas City, Missouri 64110

10. PROGRAM ELEMENT NO.
1HD621

11. CONTRACT/GRANT NO.
68-02-1728

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Monitoring and Support Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

13. TYPE OF REPORT AND PERIOD COVERED
Final

14. SPONSORING AGENCY CODE
EPA-ORD

15. SUPPLEMENTARY NOTES

16. ABSTRACT

A thorough literature search for methods of sulfate analysis has been completed. The results of the search with a very brief abstract of each method are attached as an appendix. The analytical methods have been reviewed for strengths and weaknesses, and the two most promising methods have been selected. Based on this review, the two recommended methods are the methyl thymol blue method described by A. L. Lazrus and the barium chloranilate method modified by H. N. S. Schafer and developed by R. J. Bertolacini and J. E. Barney, II. The results of this phase of the investigation have been submitted to EPA. Acceptance of the two recommended methods and approval to complete the investigation were received October 15, 1975.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Bibliographies Methodology	Sulfate Analysis Methyl Thymol Blue Barium Chloranilate Literature Search	13B

PRICES SUBJECT TO CHANGE

18. DISTRIBUTION STATEMENT Release Unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 143
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE 6.00 - 2.25

EPA Form 2220-1 (9-73)

EPA-600/4-76-008
March 1976

MEASUREMENT OF ATMOSPHERIC SULFATES: LITERATURE SEARCH AND METHODS SELECTION

by

Fred J. Bergman
Midwest Research Institute
425 Volker Boulevard
Kansas City, Missouri 64110

Contract No. 68-02-1728

Michael E. Beard
Quality Assurance Branch
Environmental Monitoring and Support Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

DISCLAIMER

This report has been reviewed by the Environmental Research Center, Research Triangle Park, Office of Research and Development, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

This program, "Measurement of Atmospheric Sulfates: Literature Search and Methods Selection," is being conducted under the Environmental Protection Agency (EPA) Contract No. 68-02-1728, which is Midwest Research Institute (MRI) Project No. 3948-C. The program is concerned with methods for analyzing the water soluble sulfates in ambient air samples. The objectives of the program were (a) to conduct a thorough literature survey, (b) to select the two most promising methods, and (c) to subject the two methods to a ruggedness test.

This is the final report of Phase I covering the literature search and the selection of the two most promising methods. The results of the literature search for methods of sulfate analysis are included as an appendix.

This program is being conducted under the management of Mr. Paul C. Constant, Jr., Head, Environmental Measurements Section of MRI's Physical Sciences Division. The principal investigator is Mr. Fred J. Bergman.

Approved for:

MIDWEST RESEARCH INSTITUTE

L. J. Shannon

L. J. Shannon, Assistant Director
Physical Sciences Division

April 2, 1976

TABLE OF CONTENTS

Page

Foreword iii

List of Tables vii

Summary. ix

Section

I Introduction 1

II Literature Search. 2

III Methods Identification 5

IV Basic Analytical Procedures. 6

V Factors Affecting the Analytical Procedure 12

VI Criteria for Method Selection. 15

VII Method Evaluation. 16

- Atomic Absorption. 16
- Chromatographic. 17
- Colorimetric 17
- Conversion-Detection 17
- Electrometric. 18
- Flame-Photometric. 19
- Fluorometric 19
- Gravimetric. 19
- Radiometric. 19
- Spectrophotometric 20
- Substituted Benzidines 21
- Turbidimetric. 21

VIII Method Selection 22

Preceding page blank

CONTENTS (Concluded)

Page

Appendix - Bibliography of Methods for Sulfate Analysis 23

Atomic Absorption 24
Chromatographic 25
Colorimetric. 27
Conversion-Detection. 61
Electrometric 65
Flame Photometric 77
Fluorometric. 78
Gravimetric 79
Nephelometric and Turbidimetric 88
Radiometric 95
Spectrophotometric. 96
Substituted Benzidines. 103
Miscellaneous - Methods 107
Miscellaneous - Books 116
Sampling. 128
Addendum. 132

LIST OF TABLES

No.	Title	Page
1	Potential Interferences Resulting from Insoluble Salt Formation at a pH of 7.0	14

SUMMARY

A thorough literature search for methods of sulfate analysis has been completed. The results of the search with a very brief abstract of each method is attached as an appendix. The analytical methods have been reviewed for strengths and weaknesses and the two most promising methods have been selected. Based on this review, the two recommended methods are the methyl thymol blue method described by A. L. Lazrus and the barium chloranilate method modified by H. N. S. Schafer and developed by R. J. Bertolacini and J. E. Barney, II.

The results of this phase of the investigation have been submitted to EPA. Acceptance of the two methods recommended and approval to complete the investigation was received 15 October 1975.

Preceding page blank

SECTION I

INTRODUCTION

Recent health effects studies have shown that the concentration of sulfate in ambient air presents a significant hazard to human health. The use of catalytic control devices in automobiles will possibly increase the level of atmospheric sulfates.

This has led to an increasing emphasis on the measurement of sulfate concentrations in ambient air. Since the data obtained may subsequently be used to set an ambient air standard for sulfates and may influence automotive standards for other emissions, it is important that the analytical methods used for sulfate analysis be reliable.

One method of determining reliability is to subject candidate methods to a ruggedness test as described by W. J. Youden and Stowe and Mayer.* The results of a ruggedness test then permit strengthening the methods and enable EPA to recommend the most reliable of the methods evaluated.

The program for accomplishing the above goals was divided into three phases. Phase I included a thorough literature search and an evaluation of the various methods with a recommendation of the two most promising methods. Phase II covers a familiarization period and a detailed method write-up for the two methods. Phase III includes the ruggedness test design and investigation and a qualitative identification of the significant and nonsignificant effects. This report presents a complete description of the work performed under Phase I of the program.

---

* Statistical Techniques for Collaborative Tests by W. J. Youden, A.O.A.C. Publications, Box 540, Benjamin Franklin Station, Washington, D.C. 20044, and Efficient Screening of Process Variables by R. A. Stowe and R. P. Mayer, *Ind. Eng. Chem.*, 58:36-40 (1966).

SECTION II

LITERATURE SEARCH

The first task conducted during this program was a thorough literature search for available methods for sulfate analysis. This search covered all available abstracts to the present time, which included: Air Pollution Abstracts, APCA Abstracts, Chemical Abstracts, and Analytical Chemistry Annual Reviews. We have also searched Analytical Chemistry, Environmental Science and Technology, Journal of APCA, and have conducted a keyword search of the Bay Area Air Pollution Library and the MRI Pollution Library. Listings of reports from the EPA Library and the National Technical Information Service were also screened. Texts covering analytical chemistry at the Linda Hall Library of Science and Technology and MRI were also examined.

A card index was compiled from the literature search. Each card contains the senior author, the article's title, a brief description of the method, and the source.

The cards were grouped by the analytical technique and each section was alphabetized by the senior author's name. The methods were grouped primarily by the method of measurement. For example, a volumetric method with a visual end-point is listed under colorimetric, but if conductivity was used it is listed under electrometric. The following is a list of the headings and the methods included in each group.

A--Atomic Absorption: Methods based on atomic absorption of either excess reactants or atomic absorption inhibition titrations.

B--Chromatographic: Methods which use paper or column separation or electrophoresis to separate anions. Methods using ion-exchange to remove interfering cations are not included in this section but are reported in the section related to the detection method.

C--Colorimetric: Methods using acid-base indicators, compleximetric colored end-points, visual turbidimetric and fluorescent optical end-points.

D--Conversion-Detection: Methods based on converting the sulfate to SO_2 or H_2S and measuring the resulting product.

E--Electrometric: Methods using either current or voltage for measurement. This includes amperometric, potentiometric, specific ion electrode and pH methods.

F--Flame-Photometric: Methods based on the direct analysis of the sulfate ion or flame emission of cations such as Ba and Pb used for indirect analysis.

G--Fluorimetric: Methods using U-V excitation and fluorescent emission for analysis.

H--Gravimetric: Methods based on the weight of a precipitate. The gravimetric methods using substituted benzidines are reported under K.

I--Radiometric: Methods using radio labeled compounds and counting techniques for analysis.

J--Spectrophotometric: Methods based on concentration measured by transmission or absorbance using U-V or visible light (200 to 1,000 nm).

K--Substituted Benzidines: Methods based on substituted benzidines regardless of the analytical detection technique. The substituted benzidine methods include gravimetric and spectrophotometric as well as procedures for preparing some of the substituted benzidines.

L--Turbidimetric: Methods based on either turbidimetric or nephelometric measurements.

M--Miscellaneous: Methods not included in the other categories.

N--Books: Listing of some of the texts which contain multiple methods of sulfate analysis. All of the methods were covered in the previous sections.

O--Sampling: Methods which contained information on collecting ambient samples. Articles which consist primarily of sampling techniques appear in this section only. When a detailed analytical method is covered in the same article, it is also indexed under the analytical group heading.

After the original search was indexed, duplicates were eliminated and the bibliographies of the more recent publications were checked to locate any missing references. The results of the survey are presented in the Appendix.

Because of the large number of articles located, the abstracts are rather cryptic to maintain a manageable document. Information which was presented in a publication title was generally not repeated in the method abstract.

SECTION III

METHODS IDENTIFICATION

The methods located during the literature search were evaluated to identify the basic analytical techniques employed. These techniques may be summarized as follows:

1. $SO_4^{-2} + Ba^{+2} \longrightarrow BaSO_4$
2. $SO_4^{-2} + Pb^{+2} \longrightarrow PbSO_4$
3. $SO_4^{-2} + (X) \longrightarrow (X)SO_4$
4. $SO_4^{-2} + Me(X) \longrightarrow MeSO_4 + (X)$
5. $SO_4^{-2} + 2Na^{+1} \longrightarrow Na_2SO_4$
6. SO_4^{-2} (physical properties)
7. $SO_4^{-2} \longrightarrow SO_2$
8. $SO_4^{-2} + H_2 \longrightarrow H_2S$

These generalized formulas describe the reactions that have been used for measuring sulfate. In most reaction types, three methods of quantitating the results are described in the published literature. The procedures used for quantitating consist of measuring the reaction product, measuring the reagent consumed or measuring the excess reagent. In some methods, the reagent consumed is determined indirectly by measuring the anion released by the reaction.

SECTION IV

BASIC ANALYTICAL PROCEDURES

This section presents a detailed discussion of the basic reactions and the methods employed for analysis.

1. $SO_4^{-2} + Ba^{+2} \longrightarrow BaSO_4$

The basic reaction relies on the addition of a barium salt to produce insoluble barium sulfate. Interferences result from the presence of any anion producing insoluble barium salts. By carrying out the precipitation at a low pH, most anion interferences can be minimized.

a. Measuring the barium sulfate: Gravimetric procedures are one of two techniques generally used for determining the barium sulfate product. Published techniques using barium are listed in the Appendix under Gravimetric and include references 406 to 468 with the exception of 423, 429, 430 and 434. These methods use reagents other than barium and are discussed elsewhere in the report. Errors, when the precipitation is carried out at a low pH, are caused primarily by the inclusion of foreign ions in the precipitate and the production of fine precipitates which are difficult to filter. A number of papers have attempted to minimize these effects. A correction for the solubility of $BaSO_4$ is sometimes applied for greater accuracy.

The second technique employed to quantitate the barium sulfate product is based on opacity.

The same basic barium precipitation reactions are employed for nephelometric (reflected light) and turbidimetric (transmitted light) procedures. The same solubility and interference problems apply when using turbidity that are associated with the gravimetric procedures.

Besides the interference problems resulting from other ions, nephelometric and turbidimetric methods require a fine, stable, uniformly sized precipitate. A considerable number of investigations have been conducted to optimize precipitation conditions.[469-525/] Under proper conditions, the system follows the Beer-Lambert law over a reasonable concentration range.[507,524/]

b. Measuring the barium used: There are numerous techniques reported in the literature for measuring the barium required for precipitation. One technique consists of measuring the excess barium. This can be accomplished by back titrating the excess barium using a wide variety of titrants. These titrants have included Trilon B,[26,243,262] K_2CrO_4 (13 references), EDTA (11 references), Na_2CO_3 (four references), K_2SO_4,[74] NH_4OH,[87] $NH_4KCr_2O_4$,[77] Na_2HPO_4,[204] and Na_2SO_4.[226] Excess barium has also been measured by atomic absorption,[1,3,4,6] flame emissions,[395-401] and emission spectrophotometry.[621]

Another measurement technique consists of adding excess barium ions, filtering the precipitate, dissolving the precipitate and titrating the barium. These procedures have employed a number of reagents to dissolve the $BaSO_4$ and titrants consisting of EDTA or the addition of sodium thiosulfate followed by an iodometric titration.

A third method of measuring barium consumption relies on the addition of a standard barium solution to produce insoluble barium sulfate. The excess barium which occurs near the equivalency point of the precipitation is then detected.

The procedure is generally titrimetric using one of several end-point indicators. Eriochrome Black T,[34] tetrahydroxyquinone (17 references), disodium rhodizonate (17 references), Alizarin Red S (eight references), nitchromazo (five references), MTB (three references), SPADNS,[54] fluorescein (three references), and thorin (13 references) have all been used. Various modifications of the basic method have been developed for end-point improvement. Photometric end-point sensing[104,187,190] has been used as well as automatic[83] spot plate[71,138,139] and high frequency oscillometric techniques.[45,53,146,171,180,194]

The end-point has also been determined amperometrically,[381] potentiometrically (21 references), and coulometrically.[357,358,359,383]

c. Measuring the anion released during precipitation: A number of procedures added a barium salt and measured the inorganic anion released by the barium sulfate precipitation. Barium chromate has been employed with the released chromate determined iodometrically (eight references) by titrating with phenylcarbazide,[148] ferrous sulfate,[97,153,240] ceric ammonium sulfate,[169] and tin chloride.[209] Barium iodate has also been used with the released iodate determined iodometrically.[38,129,236] Barium oxalate has been employed with the oxalate ion titrated using potassium permanganate.[38,147,189,213] Barium carbonate has been used with the carbonate ion determined by acidimetry,[86,243] and barium thiosulfate used as the precipitant with the released thiosulfate determined iodometrically.[156] Barium phosphate has also been employed with the released phosphate neutralized with standard sodium hydroxide and the excess hydroxide titrated with standard HCl.[159]

2. $SO_4^{-2} + Pb^{+2} \longrightarrow PbSO_4$

Most of the procedures using lead to precipitate sulfate employ either a direct titration or a precipitation followed by a determination of the lead content of the precipitate.

Nine publications determined sulfate by titrating with lead, the end-point determined using dithizone. Two publications determined lead by titrating with sodium hydroxide, adding sodium or ammonium sulfide and back titrating with sodium hydroxide.[32,120] Sulfate has also been measured by titrating with lead nitrate in the presence of KI,[168,172] or erythrosin.[55,254]

A number of publications reported sulfate analysis by precipitating lead sulfate and determining the lead content of the precipitate by titrating with EDTA[122,123,154,252] or other chelating agents[191] potassium ferrocyanide,[44,107,108] ammonium molybdate[150] or sodium carbonate.[200,255] The precipitated lead sulfate has also been analyzed by adding an excess of EDTA and titrating the excess with zinc chloride.[29,239]

Lead nitrate has been employed to precipitate lead sulfate with the end-point detected using a lead specific ion electrode.[334,372,385,392] The end-point has also been determined potentiometrically (24 references) using a Redox indicator[386] or by conductiometric and amperometric titration.

3. $SO_4^{-2} + (X) \longrightarrow (X)SO_4$

This approach employs a reaction with sulfate ions to form an organic salt or a colored complex. Two examples are the reaction of a sulfate with $FeSO_4$ in perchloric acid to form a colored complex[544,546] and the formation of a colored complex with hexamminecobalt (III) bromide $[Co(NH_3)_6]BrSO_4$.[434]

A number of procedures are reported in the literature which utilize organic sulfates. The organic reagents frequently used are benzidine or the substituted benzidines. Other potential organic materials have been evaluated. For gravimetric work, the main advantage of using the organic reagents is a reduced sulfate solubility and a corresponding increased sensitivity. These advantages are frequently coupled with a significant increase in interferences. The organic reagents form insoluble complexes with metallic salts and form insoluble salts with anions. The metallic interferences can be effectively eliminated by treating the sample with a hydrogen form ion-exchange resin but preventing anion precipitation is considerably more difficult. Phosphate, tellurite, selenate and oxalate have been reported as forming insoluble salts.[586] Of these four, phosphate appears to be the most significant interference for ambient work.

The effective removal of phosphate using calcium or zinc salts has been reported.[583]

The development of substituted benzidine as gravimetric reagents was followed by their application to nephelometric determination. The reagent commonly used was 4-amino-4'-chlorodiphenyl (CAD).[597] The problem of producing a stable precipitate when using CAD appears to be similar to those associated with $BaCl_2$, although not as severe. Fluoride is an interference at concentrations over 0.18 μg/ml. Phosphate is also an interference which may be removed according to Martin.[597]

The most promising substituted benzidine for nephelometric analysis appears to be 2-aminoperimidine.[603] This reagent was found to produce a heavy silky precipitate of uniform small particle size that did not aggregate on standing for several hours.

4. $SO_4^{-2} + Me(X) \qquad MeSO_4 + (X)$

This method utilizes metallochromic indicators containing polyvalent cations which react with sulfate to release the ligands. Barium, thorium and zirconium have all been employed.

The ligands have been employed two ways. One approach consists of reacting the sulfate with the polyvalent cations and using the excess cations to form a colored complex. The alternate approach reacts the metallochromic indicator with sulfate to release the ligands which are then measured either by a bleaching reaction or color development.

These methods have employed methyl thymol blue, a thorium borate-amaranth dye,[558,559,560] methylsulphonazo III, pyrocatechol violet,[574] and SPADNS. One method was reported based on the bleaching of a colored thorium complex rather than the development of a colored complex.[195]

The barium chloranilate method also is in this group. In this method, the insoluble barium chloranilate reacts with sulfate to produce barium sulfate and release the water soluble chloranilic acid. The released chloranilic acid is then measured.

The release of an organic component has also been employed to develop fluorescent methods. The thorium salts of morin,[402] flavonol, [403] and salicylfluorone[404,405] have been used in fluorescent methods.

5. $SO_4^{-2} + 2Na^{+1} \longrightarrow Na_2SO_4$

This procedure is based on the determination of sulfate by titration with standard base. The procedures are primarily methods for converting the salts to free acids and eliminating other acidic components. Analysis is normally accomplished by alkalimetry (10 references). Plain coulometry has been employed to give total acid equivalents and prefilters have been employed to remove major interferences. The acids have been released from the salts using hydrogen form ion-exchange resins. Sulfates have also been separated by microdiffusion, thermal decomposition, and chromatography using activated alumina.

6. SO_4^{-2} (physical properties)

These procedures rely on some physical characteristic of the sulfate. Methods have employed I-R spectrophotometry,[638,639,656] emission spectrophotrometry,[611] x-ray defraction and emission,[638,642,660] and refractive index of the precipitate.[611] Efforts have also been made to identify sulfates by crystal shape using microscopy[614,616,654] with and without color development.

7. $SO_4^{-2} \longrightarrow SO_2$

This method relies on converting the sulfate to SO_2 using hot copper[281,291,300] or tin.[283] Once the conversion is completed, the SO_2 may be measured using flame photometry,[300] spectrophotometry,[281,291,300] or conversion to $SO_4^{=}$ with H_2O_2 and measured using alkalimetry[283] or other sulfate procedure.

Sulfate may also be precipitated as perimidylammonium sulfate which is then pyrolyzed to produce SO_2 which is measured.[596]

8. $SO_4^{-2} + H_2 \longrightarrow H_2S$

There are a number of publications which convert the sulfate to H_2S which in turn is measured. A number of reducing agents have been employed which include hydrogen with a platinum catalyst,[285,301,302,304] $ZnCl_2$ + H_3PO_4,[297,303] Sn + H_3PO_4[290,296] and Ti + H_3PO_4.[295]

A number of investigators have employed hydroiodic acid for the reduction combined with formic acid and red phosphorus,[292,293] hydrochloric and hypophosphorus acids,[294] formic acid and hypophosphite,[299] acetic acid and sodium hypophosphite,[287] acetic anhydride and sodium hypophosphite,[278] and 50% hypophosphite and hydrochloric acid.[280]

The resulting hydrogen sulfide has been collected in a cadmium solution and measured gravimetrically,[284] volumetrically using mercury acetate with dithizone as an indicator,[280,295] iodine solutions[303] or using polarography.[288] Procedures have also measured the hydrogen sulfide by collecting the H_2S in zinc sulfate and measuring iodometrically[285,290,294,297,304] or collecting in zinc acetate followed by the methylene blue reaction.[286,289,292,293,299]

SECTION V

FACTORS AFFECTING THE ANALYTICAL PROCEDURE

An analytical procedure usually consists of several steps in obtaining the desired results. The weakest step in the procedure will therefore limit the results. To analyze for sulfate, one can either employ a reaction which is specific, remove or mask the interferences, or separate the sulfate ion prior to analysis.

The majority of the sulfate procedures utilize the formation of an insoluble precipitate as the detection method. The sulfate salts must be insoluble and other salts should be soluble. A review of the literature shows that barium is the best possible choice of inorganic cations available. Although lead, strontium, thorium and other cations have been employed, they will suffer from interferences resulting from the production of other insoluble salts.

The interferences resulting from the presence of various cations may be easily eliminated by treating the sample with a hydrogen form ion exchange resin. The resulting solution is then essentially a mixture of anions from which sulfate must be selectively measured. The presence of other anions essentially rules out methods based on alkalinity.

The solubility of barium sulfate is the lowest of any inorganic sulfates. Barium is therefore the inorganic reagent of choice for analyzing sulfate. There are a number of other barium salts which have low solubilities in water. These are potential interferences which are listed in Table 1 with their solubilities.

All of the barium salts in Table 1 become more soluble as the pH is decreased with barium sulfate being affected only slightly. A procedure using barium as a sulfate reagent therefore becomes essentially interference free at a low pH. An analytical procedure based on barium precipitation should therefore be performed at a low pH.

These criteria have been used to eliminate from further consideration analytical procedures using cations other than barium and the colorimetric

Table 1. POTENTIAL INTERFERENCES RESULTING FROM INSOLUBLE SALT FORMATION AT A PH OF 7.0

Potential anion Interference	Solubility in H_2O of barium salt: percent
Arsenate	0.055
Carbonate	0.002
Chromate	0.0003
Fluorosilicate	0.026
Iodate	0.033
Molybdate	0.0058
Oxalate	0.009
Phosphate	Insoluble
Selenate	0.012
Silicate	Insoluble
Sulfate	0.0002
Sulfite	0.02

procedures using barium in near neutral mediums. The same limitations apply to methods relying on the precipitation of barium sulfate to produce or release a colored product.

Colorimetric and spectrophotometric procedures using rhodizonate, tetrahydroxyquinone or indicators containing sulfo or hydroxy groups including carboxyarsenazos are used at a pH of 5.5 to 6.5. Under these conditions, most of the anions in Table 1 interfere with the procedure.

The only known indicators which can be used at a low enough pH to avoid phosphate and arsenate interferences are carboxyarsenazos with one of the -COOH or AsO_3H_2 groups replaced by an $-SO_3H$ group.

SECTION VI

CRITERIA FOR METHOD SELECTION

A requirement of this program was the selection of the two most promising sulfate methods located during the literature search. To accomplish this objective, the methods were evaluated using a set of criteria. These criteria are listed below in descending order of importance:

Precision

Interferences

Sensitivity

Accuracy

Simplicity

Time/Analysis

Automated

Equipment Cost

SECTION VII

METHOD EVALUATION

To accomplish the method evaluation and selection, the best procedure for each technique was selected. These procedures and their evaluations are presented in this section.

ATOMIC ABSORPTION

Atomic absorption measures excess barium ions remaining after sulfate precipitation. Precipitation can be carried out in acid solutions to minimize interferences. Detection limits for excess barium should be around 0.1 ppm with a precision of 5 to 7%. Some interference was associated with most of the ions investigated.[4] The strongest interference was associated with phosphate. The error produced was related to the phosphate concentration. A phosphorus level (as phosphate) of 0.125 μg added to a 6 ppm sulfate solution produced a 2% positive interference. The maximum effect was about 9% positive.

The accuracy is estimated to be plus or minus 10%. The procedure is simple. Time for each precipitation is 15 hr, however, operator time is minimal. An automated procedure has not been published. The equipment cost, which includes an AA with automatic background correction and a high speed centrifuge, is estimated to be $18,000 for the manual method.

Atomic absorption inhibition titration is an alternate method for analyzing sulfate. Its main advantage over measuring residual barium is a rapid analysis. The barium precipitation is not required, which eliminates the 15 hr precipitation and the use of a centrifuge. Experimental results indicated that the method is only applicable when the sulfate ion concentration is at least twice the combined concentration of all other ions.

In general, Christian and Feldman* have found that most anions interfere with the indirect determination (cation precipitation) using atomic absorption, the interference being in direct proportion to the concentration of all other anions. The same holds true for indirect titration using either magnesium or calcium. Interferences have been reported resulting from proteins and sugars as well as anions.

---

* Christian, G. D., and F. J. Feldman, Anal. Chim. Acta., **40**:173 (1968).

CHROMATOGRAPHIC

Methods listed under the heading Chromatographic are considered as separation techniques. A color development reaction is generally required. The technique is more qualitative than quantitative with poor precision and accuracy.

COLORIMETRIC

Following the criterion of using a barium reagent at low pH, as discussed in the previous section, eliminates most colorimetric procedures.

The use of nitchromazo[145/] as an indicator with a barium salt titration at a pH of 2.0 has the highest potential as an interference-free colorimetric procedure. Arsenate at four times the sulfate concentration and phosphate at five times the sulfate concentration produce a relative error of -1.9%. Phosphate at the same concentration as the sulfate had no effect. Information on other interferences was not presented, however, none should exist with the possible exception of silicates. The precision of the methods was not given but titration agreed within 0.3 µg of barium. The lower limit of detection was given as 0.04 mg of S as sulfate in a 10 to 15 ml sample.

The method is simple (direct titration), fast, and requires no special equipment. The procedure has not been automated but has that potential.

CONVERSION-DETECTION

These methods in general are total sulfur methods and are not specific to sulfate. Interferences would therefore be produced by sulfur, sulfides, sulfites, and thiosulfates. The procedure must therefore be combined with a separation technique prior to conversion to H_2S or SO_4. Only two methods were located which included a separation step. One method used controlled thermal decomposition for separation.[300/]

This method was developed to measure sulfuric acid aerosols. However, the authors provide information on the decomposition temperatures of other sulfates which permits, by temperature programming, measuring other sulfates. As the method is described, only sulfuric acid, ammonium sulfates and copper sulfates are decomposed and measured. Three methods were described for measuring the generated SO_2. The colorimetric method had a relative deviation of 2.2% for 23 µg of H_2SO_4. The relative deviation was

2.97% for 8.4 μg of H_2SO_4 using coulometric detection and 1.05% for 6.0 μg of H_2SO_4 using flame photometric detection. The sensitivity is more than adequate for ambient analysis. The procedure is moderately complex, requiring three steps. Time for each analysis is reported as 10 min/sample with actual analysis probably running around 30 samples/day. The method could not be easily automated and equipment cost using FPD (best precision) would be approximately $5,000.

A separation procedure has been published which precipitates perimidylammonium sulfate.[596] The precipitate is then thermally decomposed to yield sulfur dioxide which is measured by one of several techniques.

The precipitation step requires about 10 min. From the publication, it appears that separation of the precipitate is not required. This being true, the procedure would consist of precipitation, evaporation, pyrolysis and measuring the liberated SO_2 . The best results were obtained using the West-Gaeke procedure for SO_2 analysis which had a coefficient of variance of 5.3% at the 10 μg level. However, an FPD sulfur analysis could be employed with a precision of 6 to 10% at a 0.5 μg level of sulfate. The method is apparently free of any major interferences. No effects were found for phosphate, carbonate or nitrate. An earlier investigation of aminoperimidine (PDA)[603] found that a 10-fold excess of most common anions would not interfere with the sulfate precipitation. The method appears to have good precision, to be free of interferences, and to have adequate sensitivity and accuracy. The procedure is more complex than most of the other sulfate methods. Time for the analysis is reported as 4 to 5 min/sample. However, if the West-Gaeke procedure is used considerably more time would be required for a complete analysis. Automated procedures for SO_2 are available but this would require an additional capital investment. Depending on which options are selected, the equipment cost would vary from several hundred to several thousand dollars.

ELECTROMETRIC

All of the electrometric methods are based on end-point determination using primarily barium or lead as the titrant. All of the potentiometric, conductometric, and polarographic titrations suffer from a number of interferences.

The ion-selective electrodes have also been employed for sulfate analysis. Both lead and barium have been used with cation selective electrodes. The interferences produced by cations could be effectively removed using ion exchange resins. Cations listed as interferences with the lead electrode include Cu^{+2}, Hg^{+2} and Ag^{+}.[372] The anion interferences are a direct result of insoluble precipitate formation[372] and could be minimized by operating at a pH of 2.0. However, since response is related to the ionic strength of the solutions, there are inherent errors in using a specific ion electrode.

A divalent electrode was investigated as an end-point indicator for a barium titration.[334] The solubility product of barium sulfate was too large and the electrode sensitivity too low to give reliable results. Anion-responsive electrodes based on ion association extraction systems have been investigated.[318] Information on interferences indicates a significant problem.[319]

FLAME-PHOTOMETRIC

This technique appears to have no advantage over other methods for sulfate analysis. The method is based on precipitation of an insoluble sulfate and measuring the excess barium. Barium would be the reactant of choice at a low pH. Interference problems would be typical for this reaction mechanism.

FLUOROMETRIC

All of the fluorometric methods employed a thorium salt. This system suffers from significant interferences by phosphate, tungstate, molybdate, citrate, arsenate, selenate, vandate and several anions.

GRAVIMETRIC

Gravimetric procedures using barium at a low pH have been intensively investigated. The technique is still generally considered to be the most accurate. However, because of the long time required to complete the precipitation and the problem of coprecipitation, it is seldom employed. The original investigation of substituted benzidines was initiated to overcome these shortcomings, a goal which was achieved. The substituted benzidine sulfates have lower solubilities, precipitation times are shorter, and the coprecipitation problem is decreased. However, because the substituted benzidine precipitation was still rather time-consuming and suffered from interferences, all of the recent publications have employed procedures other than gravimetric.

RADIOMETRIC

All of the radiometric procedures published were employed to investigate reaction mechanisms. Their weakness as an analytical method lies in the basic problem of the precipitation reaction. All of the cations utilized for precipitation produced serious interference problems.

SPECTROPHOTOMETRIC

Three spectrophotometric methods were selected for consideration because of basic differences in the approach.

The methylthymol blue method (MTB) employs a barium precipitation reaction with an indicator which is pH sensitive and will not form the colored chelate in acidic solutions. This deficiency is at least partially controlled by conducting the precipitation at a low pH (2.6) and then raising the pH to 12.8 to form the chelate. Interferences are therefore minimized if the times allowed for precipitation and color development are carefully optimized. The procedure does suffer from a phosphate interference and also it must be conducted using automated equipment because the reagent is easily oxidized.

Data interpretation is more involved using the MTB procedure than it is with most procedures because the color reaction does not follow the Beer-Lambert law.

The barium chloranilate procedure relies on the barium precipitation reaction and measuring the released chloranilic acid. The procedure can be run as a manual spectrophotometric method or as an automated method. The greatest sensitivity is obtained using the manual procedure at 327.5 nm. Chlorides, fluorides and phosphates are listed as interferences. It is reported[575/] that by using a hydrogen form ion exchange resin and buffering to pH 1.75, the interferences are minimized. Under such conditions, 100 µg of phosphate and 50 µg of fluoride produce an error of 2% when analyzing 10 µg of sulfate. Under the same conditions, a sample containing up to 17.5 µg of chloride may be analyzed without affecting the results.

The spectrophotometric determination of sulfate using 2-aminoperimidine has been developed to cover a range of 4 to 120 ppm.[595/] The method is fast, simple, and could be automated with the proper colorimeter (305 nm). The relative standard deviation is 3.7 for 50 µg/ml of sulfate and 5.0 for 10 µg/ml. A number of interferences were investigated with 50 ppm of phosphate producing a 1% error. Large amounts of acetate, chloride, bromide, and iodide had no effect. Fluoride, nitrate, and carbonate do interfere. Fluoride at 500 µg/ml produced an error of 4% and nitrate at 500 µg/ml produced a 60% error. At 100 µg/ml, nitrate had no effect. Carbonate interferences could probably be eliminated by acidifying the solution.

SUBSTITUTED BENZIDINES

The methods employing substituted benzidines are discussed in this section under the measurement techniques employed.

TURBIDIMETRIC

Two methods were selected for consideration which were based on turbidity.

The turbidimetric method normally encountered employs the barium precipitation reaction. Barium chloride is normally used in an acid medium which eliminates most interferences. There is no need to remove either cations or anions. Silica and phosphate, in large quantities as well as turbidity and color, are the only reported interferences. Phosphate is not normally present in sufficient quantities to cause an interference. A drift in the base line caused by $BaSO_4$ buildup is also encountered when using an automated method. The major disadvantage of this procedure is poor precision. A number of stabilizing materials have been investigated in an effort to obtain improved precision. There are a number of factors which influence the size of the particles precipitated and therefore the precision of the method. These factors include sulfate concentration, reagent concentration, reaction temperature, presence of other ions, cleanliness of the system, age of the barium reagent, and precipitation time. Good results are therefore closely related to the operator's skill. Precision, as standard deviation, varies from 1.78 µg/ml analyzing 9.2 µg/ml of sulfate to 11.8 µg/ml analyzing 19.9 µg/ml of sulfate.[481/]

A second turbidimetric procedure uses 2-aminoperimidine (PDA) as the precipitant. This reagent reacts with sulfate to produce a heavy white silky precipitate.[603/] The particle size is primarily less than 2 µ across. The particles do not aggregate and the solubility of the precipitate is very low. The procedure is capable of easily detecting 0.2 ppm and has the potential of detecting as low as 0.05 ppm of sulfate. The precipitation is completed in 1 to 2 min. In the 0.25 to 1 ppm range, it was reported there was no increase in opacity after 5 min.

The PDA is susceptible to oxidation and precaution should be taken to avoid undue exposure. The procedure does suffer from some interferences.

The major problem is with fluorides and phosphates. Analyzing a 0.75 µg/ml sulfate sample, 1 µg/ml of fluoride produces an error of 10% and 1 µg/ml of phosphate produces an error of 25%.

SECTION VIII

METHOD SELECTION

Based on the discussion presented in the previous section, the following methods were selected for final consideration as the most promising:

- Volumetric using nitchromazo;
- Conversion using 2-aminoperimidine and detection using West-Gaeke;
- Spectrophotometric using methyl thymol blue;
- Spectrophotometric using barium chloranilate;
- Spectrophotometric using 2-aminoperimidine; and
- Turbidimetric using 2-aminoperimidine.

A final review was made and four methods were eliminated. The volumetric method was eliminated because of a lack of information on the lower limit of detection, precision, accuracy, and interference effects. The conversion-detection method using 2-aminoperimidine was eliminated primarily because of its complexity and the lack of supporting data. The turbidimetric and spectrophotometric methods using 2-aminoperimidine methods were eliminated because of potential interferences.

It therefore appears that the most promising methods at present are those using MTB and barium chloranilate. The automated MTB procedure reported by Lazrus[563/] is recommended. The barium chloranilate method does not have sufficient sensitivity at 530 nm using the automated procedure. We therefore recommend as the second method, the manual procedure with measurements made using either the 530- or 310-nm absorption peaks as described by Schafer.[575/]

APPENDIX

BIBLIOGRAPHY OF METHODS FOR SULFATE ANALYSIS

ATOMIC ABSORPTION

1. Borden, F. Y., "Indirect Method for the Measurement of Sulfate by Barium Absorption Spectrophotometry," *Soil Sci. Soc. Amer.*, 34(4):705-706 (1970).

   Excess Ba by atomic absorption.

2. Christian, G. D., "Determination of Nonmetals by Atomic Absorption Spectrophotometry," *Anal. Chem. Acta*, 49(2):173-179 (1968).

   $SO_4^=$ causes proportional decrease in Ca 4226 Å line

3. Dunk, R., "Determination of Sulfate by Indirect Atomic Absorption Spectroscopy," *At. Absorption News Letter*, 8(4):79-81 (1969).

   AA measurement of Ba after precipitation of $SO_4^=$

4. Forbes, E. A., "Determination of Microgram Amounts of Sulfate by Emission Spectroscopy of Barium with N_2O-Acelytene Flame," *Analyst*, 98(1168):506-511 (1973).

   Method for 0.5 to 10.0 ppm by Ba emission at 553.55 nm; sensitive and relatively free of interferences.

5. Lin, C. I., "Determination of Phosphate, Silicate, and Sulfate in Natural and Wastewater by Atomic Absorption Inhibition Titration," *Anal. Chem.*, 44(13):2200-2204 (1972).

   Simultaneous detection of silicate, phosphate, sulfate 0 to 30 ppm $SO_4^=$; Titrate $SO_4^=$ with metal cation, monitoring AA signal for cation (use $Mg Cl_2$).

6. Mansell, R. E., "Industrial Applications of AAS (Atomic Absorbtion Spectroscopy)," *Amer. Lab.*, (3):31-32, 34 (1970).

   Indirect determination of SO_3 using a barium salt in air near sulfonating process. A brief description of methods, and general usefulness.

CHROMATOGRAPHIC

7. Ackermann, G., "Quantitative Paper Chromatography of Inactive Substances Through Radioactive Additions," Talanta, 15(1):63-71 (1968).

Radiometric measurement by adding constant quantity of active sulfate

8. Brezgunova, I. N., "Thin-Layer Chromatography of Anions," Zh. Fiz. Khim., 45(7):1785-1787 (1971).

TLC method for separation of phosphate, sulfate, halide, and polythionate anions of organic and inorganic compounds.

9. Canic, V. C., "Thin-Layer Chromatographic Separation of Anions on Starch," Fresenius Z. Anal. Chem., 229(2):93-96 (1967).

Qualitative detection.

10. d'Ans, J., "Use of Anion Exchangers in Analytical and Preparative Chemistry," Chem-Ztg., 76:841-844 (1952).

Nonaqueous solvents and anion resins.

11. De Souya, J. A., "Inorganic Analysis by Electrophoresis," Rev. Quein. Ind., 42(489):11-15 (1973).

Separation of 49 inorganic ions with very simple equipment as described.

12. Handa, A. C., "Microdetermination of Sulfide, Sulfite, Sulfate, and Thiosulfate by Thin-Layer Chromatography and Ring Colorimetry," Talanta, 20(2):219-222 (1973).

TLC on microcyrstalline cellulose; determined by ring colorimetry.

13. Koscielny, J., "Separation of Selenites, Sulfates, and Tungstates in the Presence of Condensed Phosphates," Pr. Nauk. Wyzsz. Szk. Ekon. Wroclaw., 23:205-210 (1970).

Paper chromatographic separation as molybdosulfate formed under UV radiation.

14. Lewandowsky, A., "Quantitative Analysis of Anions with Filter Paper Containing Anion Exchangers," *Roczniki Chem.*, **30**:559-567 (1956).

    Ion Exchange Paper Chromatography Cl, NO_3, SO_4

15. Lowe, L. E., "The Separation and Determination of Organic and Inorganic Sulfate in Soil Extracts," *Can. J. Soil Sci.*, **46**(1):92-93 (1966).

    Column of Sephadex elute with borate buffer. Good recovery above 10 ppm.

16. Nakano, S., "Behavior and Separation of Sulfate and Fluosilicate by Paper Chromatography," *J. Chem. Soc. Japan*, **75**:328-330 (1954).

    Two parts NH_4OH to eight parts MeOH recommended as solvent; successful separations when Na salts used.

17. Rudnicki, R., "A New Color Reaction for the Detection of Sulfate and Pyrosulfate Ions on Paper Chromatograms," *Chem.Anal.*, **5**:769-744 (1960).

    Paper chromatographed and developed with Hanes-Isherwood reagent. Separated all sulfur compounds.

18. Tokutomi, M., "Electrophoresis of Inorganic Anions on Anion-Exchange Paper," *Bunseki Kagaku*, **21**(1):81-87 (1972).

    Anion migration was greater than on filter paper at pH 4.0 and 7.0 using H_3HO_4-Na_2HPO_4 at 20 mA/2.5 cm.

19. Tsitovich, I. K., "Organic Reagents and Concentration of Ions by Means of Ion-Exchange Resins," *Trudy Komissii Anal. Khim., Akad. Nauk SSSR Inst. Geokhim. i Anal. Khim.*, **11**:411-417 (1960).

    $SO_4^=$ determined as $H_2NC_6H_4C_6H_4NH_2 \cdot H_2SO_4$

20. Witkowski, H., "Filter Paper with Cation Exchangers," *Roczniki Chem.*, **30**:549-557 (1956).

    Ion Exchanger Paper Chromatography

21. Zamfir, J., "Analysis of Mixtures of Sulfur Anions Labeled with Sulfur-35," *Rev. Roum. Chim.*, **13**(2):219-223 (1968).

    Separation of Na_2, SO_3, Na_2S, and Na_2SO_4 investigated using TLC, EP and column chromatography. TLC and EP did not work. Na_2S could be separated on Al_2O_3. Separation of Na_2SO_3 from Na_2SO_4 not investigated.

COLORIMETRIC

22. Abrahamezek, E., "Titrimetric Microdetermination of 0.001 N Sulfate Solutions with Sodium Rhodizonate as Indicator," *Mikrochim. Acta*, **1**:354-363 (1937).

    Titration with Ba^{++}.

23. Akiyama, T., "Direct Titration of Sulfate," *Kyota Yakka Daigaku Gakuho*, **5**:48-50 (1957).

    Titration with $Ba(ClO)_4$ and thorin.

24. Alicino, J. F., "Microvolumetric Method for Determination of Sulfur in Organic Compounds," *Anal. Chem.*, **20**:85-86 (1948).

    Solution + NaOH, EtOH, and dipotassium rhodizonate; titrated with $BaCl_2$ until color persists.

25. Andrews, J. R., "Volumetric Barium Chromate Method for Sulfates," *Ind. Eng. Chem., Anal. Ed.*, **3**:361-362 (1931).

    Titration with ferrous ammonium sulfate; back titrate with permanganate.

26. Antonova, A. A., "Rapid Complexometric Method for Determining Sulfate Ion in Potash," *Steklo i Keram*, **19**(12):23-24 (1962).

    Acidify (pH of 6); add $BaCl_2$, Na rhodizonate, pH 10 buffer, and alkali blue indicator. Titrate with Triton B.

27. Archer, E. E., "Titrimetric Determination of Sulfate with Lead Nitrate as Titrant and Dithizone as Indicator," *Analyst*, **82**:208-209 (1957).

28. Asada, T., "Determination of Phosphate and Sulfate by the Ion-Exchange Method," *Bunseki Kagaku*, **6**:100-101 (1957).

    Using "Amberlite IR-120" and NaOH titration.

29. Ashbrook, A. W., "Volumetric Determination of Sulfate," *Analyst*, **86**: 740-744 (1961).

    $SO_4^=$ precipitated as $PbSO_4$ by $Pb(NO_3)_2$ from aqueous EtOH; precipitate dissolved in EDTA, excess EDTA determined by $ZnCl_2$ titration, Eriochrome Black T indicator.

30. ASTM, "Standard Methods of Test for Sulfate Ion in Water and Waste Water (D516); Method C - Volumetric Method," Annual Book of ASTM Standards, 31:427,430-433 (1974).

Details of $BaCl_2$-thorin titration.

31. Atkinson, H., "The Volumetric Determination of Soluble Sulfates by Means of Barium Chloride and Potassium Stearate," Analyst, 50:590-600 (1925); Analyst, 51:81-82,140-141 (1926).

$BaCl_2$ precipitation; add stearate solution; back titrate with $BaCl_2$ using BHD indicator or bromothymol blue.

32. Babkin, M. P., "Colorimetric Methods for the Determination of Sulfates," Lab. Prakt., 6:19-21 (1939).

Benzidine method had errors as much as 50%. Precipitate as $PbSO_4$ in dilute AcOH and EtOH. Dissolve in NaOH and add alkaline sulfide to color; 10% error.

33. Babko, A. K., "Color Reactions for Sulfate Ion," Trudy Komissii Anal. Khim., Akad. Nauk S.S.S.R., Inst. Geokhim. i Anal. Khim., 11:309-322 (1960).

Colored complexes of Zr, Th, and Ce(III) with alizarin, alizarin S, Red Acid S., Eriochrome Black 7, aluminon, stilbazo, stibbnaphthazo, Acid Chrome Blue K (I), and acid chrome dark blue studied. EtOH or acetone enhances. $ZnNO_3$ and Acid Chrome Blue K solution mixed with HCl. Add 40% acetone to sample and measure color change. 0.2 µg/ml.

34. Bakács, E., "A Fast Titrimetric Method for the Detection of Sulfate with Barium Chloride," Magyar Kém. Folyóirat, 61:48-50 (1955).

Direct titration of $SO_4^=$ with 0.01 M $BaCl_2$ in EtOH. Eriochrome Black T with sequestered Mg ion indicator. Titrated with NH_4OH, methyl red indicator.

35. Bakács, E., "Fast Titrimetric Method for the Determination of Sulfate Ions," Magyar Kém. Folyóirat, 62:135-139 (1956).

Titration with $BaCl_2$ and thorin.

36. Balakhovskii, S., "Volumetric Method for the Microchemical Determination of Sulfates," *Z. anal. Chem.*, **86**:344-346 (1931).

Sulfate + $BaCl_2$. Titrate with K_2CrO_4. Phenol red, thymol blue, or cresol red indicator (any one).

37. Banerjee, D. K., "Determination of Diethyl Sulfate, Ethyl Hydrogen Sulfate, and Sulfuric Acid in Mixtures," *Anal. Chem.*, **36**(10):2016-2020 (1964).

Ethyl hydrogen sulfate and sulfuric acid determined by titration with $N(C_4H_9)_4OH$. Diethyl sulfate is hydrolyzed at 130°C and H_2SO_4 formed is titrated with aqueous base.

38. Banyai, E., "The Use of Precipitation Exchange Reactions in Analytical Chemistry," *Acta Chim. Acad. Hung.*, **8**:383-94 (1956).

$SO_4^=$ exchange with $Ba(IO_3)_2$, BaC_2O_4, and $BaCrO_4$. Iodate and chromate determined iodometrically; oxilate with $KMnO_4$.

39. Bartoshevich, E. I., "Rapid Method for Determining the Sodium Sulfate Content in a Complex Solution," *Maslo-Zhir. Prom.*, **35**(2):39-40 (1969).

Neutralize acid; add $BaCl_2$. Titration with K_2CrO_4, methyl red indicator.

40. Basargin, N. N., "Analytical Use of Nitchromazo, A New Indicator for Barium," *Metody Anal. Khim. Reaktivov Prep.*, (12):97-102 (1966).

$BaCl_2$ titration with Nitchromazo indicator.

41. Baxi, D. R., "Estimation of Sulfate by Ion-Exchange Method," *Salt Res. Ind.*, **4**(4):130-134 (1967).

Ion-exchange $SO_4^=$ to H_2SO_4. Titrate with NaOH.

42. Behr, I., "Simultaneous Analysis by an Ion-Exchange Method of Phosphates, Sulfates and Chlorides," *Bull. Research Connal Israel*, **5A**:259-262 (1958).

Converts $SO_4^=$ to acid with ion exchange. Phosphates and chloride determine volume and $SO_4^=$ by difference.

43. Belcher, R., "Indirect Titrimetric Determination of the Sulfate Ion with Ethylenediaminetetraacetic Acid," *Chemistry and Industry*, pp. 850-851 (1954).

Acidified sulfate + $BaCl_2$; add excess of EDTA; titrate with $MgCl_2$.

44. Belcher, R., "New Method for Titration of Sulfate," Chem. Anal., 17(3): 497-501 (1972).

Titration with 0.05 M $Pb(NO_3)_2$; back titrate with 0.01 M $K_4Fe(CN)_6$.

45. Bien, G. S., "High-Frequency Titration of Micro Quantitites of Chloride and Sulfate," Anal. Chem., 26(5):909-911 (1954).

Titration with $Ba(OAc)_2$ with a chemical oscillometer.

46. Birstein, G., "Titrimetric Determination of Aluminum Sulfate and Sulfuric Acid Present Together," Przemyst Chem., 18:317-321 (1934).

Titration with $Ba(OH)_2$. Thymol blue indicator.

47. Bond, R. D., "Determination of Low Concentrations of Sulfate with Barium Chloride and Ethylenediaminetetraacetic Acid," Chemistry and Industry, pp. 941-942 (1955).

Ba precipitation with boiling; titration with EDTA and Eriochrome Black T as indicator.

48. Bosch, F. de A., "New Detection for Barium and Sulfate Ion. I. Determination of Barium by Iodoimetry," Anales real. soc. españ. fis. y quim., 52B:187-198 (1956).

Sulfate + $BaCl_2$, add $Na_2S_2O_3$. Titrate with I_2.

49. Bovee, H. H., "Spectro-Visual Method for Determining End Points, Application to Titration of Soluble Sulfate," Anal. Chem., 29:1353-1355 (1957).

Titration with $BaCl_2$, tetrahydroxyquinone indicator. Light transmitted by Wratten filter No. 45, End point green ⟶ blue for $SO_4^{=}$-BaCl titration.

50. Bozhevol'nov, E. A., "Determination of Sulfate in Water, Acids, and Salts with Fluorexon," Metody Analizo Khim. Reaktovov i Preparatov, Gos. Kom. Sov. Min. S.S.S.R. po Khim., (4):131 (1962).

Sample titrated with EDTA in UV light until solution matches fluorescence of blank; sample evaporated with Ba, KOH, and Fluorexon in KCl.

51. Briwal, A. A., "Change in Jellinek's Method for the Determination of Sulfate," Z. Anorg. Allgem. Chem., 156:210-212 (1926).

Add $BaCl_2$; titrate excess with K_2CrO_4. Methyl red indicator.

52. Bruno, A., "Determination of Sulfates in Solution by Physico-Chemical Volumetry," Compt. Rend., 154:984-986; Ann. Fals., 5:237-239 (1912).

Determination in wine; titration with $Ba(OH)_2$.

53. Bruno, E., "Oscillometric Determination of a Small Quantity of Sulfates," Rass. Chim., 17(5):216-219 (1965).

Benzidine-HCl in iso-PrOH titration ≤ NaOH; sensitive to 9 μg/ml.

54. Budesinsky, B., "Determination of Sulfur and Sulfate by Titration with Barium Perchlorate. Comparison of Various Color Indicators," Anal. Chim. Acta, 39(3):375-381 (1967) and Anal. Chem., 210:161 (1965).

4,5-Dihydroxy-3,6-bis(p-methyl-o-sulfophenylazo-naphthalene)-2,7-disulfonic acid (Sulfonazo II) superior to thorin.

55. Burg, W. V., "Direct Titration of Sulfate - Erythrosin as Internal Indicator," Ind. Eng. Chem., Anal. Ed., 11:28-30 (1939).

$Pb(NO_3)_2$ titration.

56. Caldwell, W. E., "Reduction Reactions with Calcium Hydride. I. Rapid Determination of Sulfur in Insoluble Sulfates," J. Am. Chem. Soc., 51:2936-2942 (1929).

Iodometric titration.

57. Callan, T. P., "Determination of Sulfur in Organic Compounds. Oxidation of Sulfur of Cystine and Methionine, Combination of Parr Oxidation Bomb and Acidimetric Benzidine Method, and Determination of Small Amounts of Sulfur Compound Present as Contaminant in Organic Material," Ind. Eng. Chem., Anal. Ed., 13:450-455 (1941).

S to H_2SO_4 (benzidine sulfate method); S oxidized with $KMnO_4$; $SO_4^{=}$ as $BaSO_4$.

58. Casini, A., "Complexometric Determination of the Sulfate Ion," Ann. Chim., 46:697-702 (1956).

Excess $BaCl_2$ titration with EDTA. Naptholphthalein indicator.

59. Ceausescu, D., "Improvement of the End Point Determination in the Titrimetric Determination of Sulfates," Rev. Chim., 10:538 (1959).

Ba^{++} titration, Na alizarin sulfonate indicator. Methylene blue as contrast component.

60. Ceausescu, D., "Indirect Determination of Sulfates in Water by Titration with Potassium Stearate by Using Eriochrome Black T as Indicator," Acad. rep. populare Romine Baza cercetari stiint. Timisoara Studii cercetari stiint., Ser. stiint. chim., 5(1-2):77-81 (1958).

$SO_4^{=}$ precipitates excess Ba. Titrate excess with K stearate.

61. Ceausescu, D., "Indirect Determination of Sulfates in Water by Titration with Potassium Stearates or Palmitates After Elimination of Calcium and Magnesium," Acad. rep. populare Romine Baza cercetari stiint. Timisoara Studii cercetari stiint, Ser. stiint chim., 7:37-42 (1960).

$SO_4^{=}$ determined by $BaCl_2$ precipitation; titrate excess reagent with K stearate or palmitate in presence of either phenolphthalein or Eriochrome Black T as indicator; Ca and Mg interfere.

62. Ceausescu, D., "Rapid Determination of Sulfate, Chloride, and Nitrate Ions in Water in a Single Sample," Z. anal. Chem., 165:424-428 (1959).

$HClO_4$, $BaSO_4$, EtOH, and I added and titrated with $Ba(ClO_4)_2$.

63. Chalmers, A., "Volumetric Sulfate Determination. Rapid Method for Determining Sulfur in Organic Compounds," Ind. Eng. Chem., Anal. Ed., 4:162-164 (1932).

$S \xrightarrow{O} SO_4$. Add $BaCl_2$; titrate with Na_2CO_3, phenolphthalein indicator.

64. Chaque, A. R., "Application of Adsorption Indicators in Volumetric Precipitation," Anales guim. y farm., pp. 4-8, 11-14. In Rev. quim. farm., 24:4-14, Santiago, Chile (1945).

Investigation of indicators for Ba^{++} titration.

65. Chatron, "Microdetermination of Sulfates. Application to Sulfur and Total Bases in Serum," Bull. Soc. Chim. Biol., 13:300-325; J. Pharm. Chim., 13:244-254,321-327,425-435 (1931).

Precipitated as benzidine-SO_4. Titrate with NaOH, bromothymol blue indicator.

66. Chirkov, S. K., "Volumetric Determination of Water-Soluble Sulfates by the 'Soda' Method," *Zavodskaya Lab.*, **3**:420-424 (1934).

$SO_4^=$ precipitated with $BaCl_2$; excess $BaCl_2$ titrated with Na_2CO_3 against phenolphthalein; ± 0.002%; optimum $SO_4^=$ concentration 0.1 to 0.15%.

67. CIBA, Ltd., "Analytical Procedure with Derivatives of Acid-Base Indicators," CIBA, Ltd., Swiss 298,194, 1 July 1954 (Cl. 67).

3,3'',5',5''-tetrakis[(bis-carboxymethyl amino) methyl] phenolphthalein used to titrate excess Ba from $BaCl_2$ addition.

68. Ciurlo, R., "Chelatometric Micro Determination of Sulfate in Small Quantities," *Atti. Soc. Pleoritana Sci. Fis. Mat. Natur.*, **12**(3-4): 537-544 (1966).

EDTA - Excess titrated with Mg in 0.1% EtOH. Eriochrome Black T indicator.

69. Commins, B. T., "Determination of Particulate Acid in Town Air," *Analyst*, **88**:364-367 (1963).

Filter sample titration with sodium tetraborate to ~ pH 7.

70. Cuthbertson, D. P., "The Inorganic Sulfate Content of Blood," *Biochem. J.*, **25**:1237 (1931).

Benzidine-Thymol.

71. Damerell, V. R., "New Volumetric Method for Determination of Sulfate," *Ind. Eng. Chem., Anal. Ed.*, **6**:19-21 (1934).

$BaSO_4$ precipitated; time measured for yellow coloration of turpeth in $Hg(NO_3)_2$ on spot plate.

72. Davey, W., "Analytical Applications of Sodium Lauryl Sulfate. II. The Volumetric Determination of Sulfates," *J. Appl. Chem.*, **5**:474-476 (1955).

Determination of $SO_4^=$ by EDTA method; excess Ba precipitated with sodium lauryl sulfate; excess sodium lauryl sulfate precipitated with a quaternary ammonium salt.

73. Denk, G., "Alkalimetric Determination of Calcium, Strontium, Barium and Sulfate," *Z. anal. Chem.*, **137**:99-104 (1952).

Titration near the boiling point with Na_2CO_3.

74. De Zombory, L., "Volumetric Determinations of Sulfate with Sodium Rhodizonate as an Indicator," *Magyar Kém. Folyóirat*, **41**:189-192 (1935).

$BaCl_2$ precipitation; titrate with K_2SO_4 using Na rhodizonate as indicator.

75. Dittrich, S., "Microdetermination of Sulfate," *Anales Fac. Quim. Univ. Rep. Oriental Uruguay*, **6**:107-114 (1960).

Benzidine; titration to phenol red end point; anions precipitated by benzidine, oxidizing substances, and certain others interfere.

76. Dollman, G. W., "Determination of Sulfate and Phosphate in Water by Ion-Exchange-Titrimetric Method," *Environ. Sci. Tech.*, **2**:1027-1029 (1968).

Ion-exchange $SO_4^=$ to H_2SO_4. Titrate with NaOH.

77. Dominikiewicz, M., "Titrimetric Determination of Sulfates," *Bull. trav. dept. chim. inst. hyg. etat*, **31**(1):3-6; *Przemyst Chem.*, **14**:241-245 (1930).

$BaCl_2$ titration with NH_4K Chromate. Benzidine indicator.

78. Dragusin, I., "Complexometric Determination of Sulfates in the Presence of Calcium and Magnesium," *Rev. Chim.*, **12**:303-304 (1961).

Dual EDTA titration to obtain $SO_4^=$ by difference; uses Na rhodizonate as indicator.

79. Dubois, L., "General Method of Analysis for High Volume Air Samples. I. Sulfate and Sulfuric Acid," *Mikrochim. Acta*, (6):1268-1275 (1969).

Titration with $Ba(ClO)_4$ and thorin. Includes alternate filter extraction.

80. Dubois, L., "The Determination of Sulfuric Acid in Air: A Specific Method," *Mikrochim. Acta*, pp. 269-279 (1969).

$SO_4^=$ determined by barium perchlorate-thorin titration.

81. Effenberger, M., "Chelatometric Determination of Sulfates in Water with Calcein as Indicator," *Chem. Listy*, **52**:1501-1505 (1958).

Excess $BaCl_2$ titrated with NaEDTA, calcein indicator.

82. Ekedahl, E., "A Volumetric Method for the Determination of Sulfate Ions," *Svensk Kem. Tid.*, **58**:177-179 (1946).

Treatment of sulfate ions with Na_2CO_3. The resulting carbonate is dissolved in std. HCl and excess titrated with NaOH.

83. Ellis, W. G., "A Simplified Automatic Photometric Titrator Applied to the Titration of Microgram Amounts of Sulfate," *U.S. At. Energy Comm.*, TID-14741, (1961).

Automatic photometric titration of $SO_4^=$ with $Ba(ClO_4)_2$. Thorin indicator. Well-defined end points with 50 to 200 µg $SO_4^=$ in cell.

84. Elsermann, E., "Iodometric Titration of Sulfate," *Z. anal. Chem.*, **134**: 96-99 (1951).

Sulfate and $BaCrO_4$ in $HClO_4$, add KI, titrate with $Na_2S_2O_3$.

85. Eriksen, T. E., "Determination of Small Quantities of Sulfate and Thiosulfate in Aqueous Solution of Sulfur Dioxide," *Acta Chem. Scand.*, **26**(8):3333-3336 (1972).

Column chromatography. $Ba(ClO_4)_2$ titration. HSO_3 masked with H_2CO.

86. Erlich, J., "Volumetric Determination of Sulfate Ion," *Ann. Chim. Anal., Chim. Appl.*, **2**:214-215 (1920).

Treatment of sulfate with $BaCO_3$ followed by titration of excess carbonate with 0.1 N H_2SO_4 in presence of Helianthin.

87. Erzsébet, P., "Rapid Titrimetric Determination of Sulfate Ions with Barium Chloride as a Measuring Solution," *Magyar Kém. Folyóirat*, **61**:48-50 (1955).

Titrate with NH_4OH using methyl red indicator.

88. Flaschka, H., "The Ethylenediamine Titration: Applications III," *Chemist Analyst*, **47**:52-56 (1958).

Discussion.

89. Foldesi, K., "Rapid Method for Sulfate Determination," *Bőr - 'es Cipő tech.*, **11**:20-23 (1961).

Precipitation in solvent solution with $BaCl_2$ and titration of the excess with EDTA using Eriochrome Black T indicator.

90. Foster, M., "Volumetric Detection of Sulfate in Water," Ind. Eng. Chem., Anal. Ed., 8:195 (1936).

Iodometric titration. Barium chromate back titration with thiosulfate.

91. Freeland, M. Q., "Direct Titration of Sulfate," U.S. Atomic Energy Comm. ISC 667, pp. 1-32 (1956).

Titration with standard Ba solution using Alizarin Red S or Thorin as an indicator.

92. Fritz, J. S., "Determination of Sulfate," Anal. Chem., 26(10):1593-1595 (1954).

Titration with standard Ba solution ($BaCl_2$ or $Ba(ClO_4)_2$) in 30 to 40% EtOH using Alizarin Red S indicator.

93. Fritz, J. S., "Rapid Microtitration of Sulfate," Anal. Chem., 27(9): 1461-1464 (1955).

Titration with $Ba(ClO)_4$ in 80% alcoholic solution using thorin indicator.

94. Fritz, J. S., "Titration of Sulfate Following Separation with Alumina," Anal. Chem., 29(1):158-161 (1957).

Titration with $Ba(ClO)_4$ using thorin indicator.

95. Fukutomi, T., "Modification of a Spot Test for Sulfate Ion," Anal. Chem., 31(6):1118 (1959).

Addition of $BaCl_2$ produces pH of 9.4; recommends use of thymolphthalein for end point.

96. Funasaka, W., "A Rapid Method for the Determination of the Sulfate Radical with an Ion Exchanger," J. Chem. Soc. Japan, Ind. Chem. Sect., 54:355-357 (1951).

H_2SO_4 titration with NaOH. Trivalent ions do not interfere.

97. Geilmann, W., "Microchemical Determination of Sulfate by the Chromate Method," Z. anal. Chem., 139:412-423 (1953).

Indirect-exchange titration of chromate with $FeSO_4$ and "ferroion" indicator.

98. Geilmann, W. "Notes on Microchemical Volumetric Analysis. I.," *Z. Anorg. Allgem. Chem.*, **167**:113-127 (1927).

Discussion of methods and procedures.

99. Germuth, F. G., "Volumetric Method for Determination of Sulfate Ion," *J. Am. Water Works Assoc.*, **19**:607-609 (1928).

Precipitation by $BaCl_2$, back titration with K_2CrO_4 using $Pb(NO_3)_2$ as outside indicator.

100. Geyer, R., "Sulfate Titration with Barium Chloride and Adsorption Indicators," *Z. anal. Chem.*, **146**:174-181 (1955).

Na-alizarin sulfate indicator.

101. Geyer, R., "Volumetric Determination of Sulfate in Water," *Z. anal. Chem.*, **158**:418-421 (1957).

Na-alizarin sulfonate indicator. Ion exchange column.

102. Giblin, J. C., "Volumetric Method for the Determination of Barium and Sulfates," *Analyst*, **58**:752-753 (1933).

Titration with $BaCl_2$ using Na Rhodizonate indicator.

103. Goday, S. R., "Iodometric Determination of Sulfates," *Bol. Farm. Militar*, **13**:361-364 (1934); *Chimie and Industrie*, **34**: 792.

Modifications of Huiman's method; $BaCl_2$ precipitation with K_2CrO_4 titration.

104. Goddu, R. F., "Photometric Titrations," *Anal. Chem.*, **26**(11):1740-1746 (1954).

Discussion.

105. Grant, J., "Summarized Methods of Analysis. III. The Sulfate Ion," *Chem. Products*, **2**:125-129 (1939).

Review of volumetric methods using benzidine, $BaCl_2$, $BaCrO_4$, $Pb(NO_3)_2$, $BaCO_3$, and BaC_2O_4.

106. Grant, J., "Summarized Methods of Analysis. IV. The Sulfate Ion, Quantitative Methods-Colorimetric," Chem. Products, 2:157-160 (1939).

General procedures with benzidine; H_2O_2 and $FeCl_3$; napthaquinonesulfonate; and $BaCrO_4$.

107. Gregorowicz, Z., "Indirect Volumetric Determination of Anions with Variamine Blue Indicator," Anal. Chim. Acta, 23:299 (1960).

$PbSO_4$ precipitate; titrate excess Pb with $K_3Fe(CN)_6$ and Variamine Blue acetate solution.

108. Gregorowicz, Z., "Oxidation-Reduction Indicators in the Indirect Volumetric Determination of Anions. Determination of Sulfate Ions with Lead(II) Nitrate," Z. anal. Chem., 177:91-97 (1960).

$PbSO_4$ precipitate; excess Pb titrated with $K_4Fe(CN)_6$ using Variamine Blue indicator.

109. Grigor'ev, P., "Volumetric Determination of the Sulfate Ion," J. Chem. Ind., 7:1004-1006 (1930).

Titration with Pb^{++} with KI indicator.

110. Gwilt, J. R., "Analytical Applications of Sodium Lauryl Sulfate. I. The Volumetric Determination of Barium," J. Appl. Chem., 5:471-474 (1955).

Ba precipitation by Na lauryl sulfate; excess Na lauryl sulfate titrated with quaternary ammonium compound.

111. Haase, L. W., "Investigation of the Benzidine Method for Determining Sulfuric Acid," Z. Angew Chem., 40:595-599 (1927).

Found Raschig method (see 202) good only above 30 mg/liter.

112. Hallett, L. T., "Microdetermination of Sulfate Obtained from Combustion of Organic Compounds. Tetrahydroxyquinone as an Indicator in a Volumetric Method," Ind. Eng. Chem., Anal. Ed., 12:360-363 (1940).

$BaCl_2$, pH 6.5 to 7.0, temperature 15 to 25°C, end point observation made by transmitted light and color compared with 2 layers of Wratten No. 21 filter, Br instead of H_2O_2 for oxidation.

113. Hamburger, H. J., "Contribution to Microvolumetric Analysis. II. Quantitative Determination of Small Quantities of Sulfate," Proc. Acad. Sci. Amsterdam, 19:115-125 (1916).

Precipitate with $BaCl_2$.

114. Hamburger, H. J., "New Methods for Quantitative Chemical Analysis. II. Microvolumetric Determination of Very Small Amounts of Sulfate," Sitz. d. Koninklyke Akad. van Wefenschoppen te Amsterdam Ap. 28'16 Biochem. Z., 77:168-188 (1916).

Precipitate with $BaCl_2$.

115. Harada, H., "Determination of Sulfate Ion by Chelating Titration," Tokyo to Ritsu Eisei Kenkyusho Nenpo, 13:195-209 (1961).

NaEDTA titration (Eriochrome Black T indicator) after conversion of Ba to Mg via MgEDTA.

116. Hauser, O., "The Sulfate Determination with Barium Chromate," Mitt. Chem. Forsch.-Inst. Wirtsch. Österr., 9:1-2 (1955).

$BaSO_4 + BaCrO_4$ precipitate; titration of I by $Na_2S_2O_3$.

117. Herrig, H. J., "Complexometric Determination of Sulfur in Combustible Complexes," Brennstoff-Chem., 42:355-356 (1961).

$BaCl_2$. Excess Ba titrated using "Titriplex-III" (Merck); phthalein purple indicator.

118. Hibbard, P. L., "The Volumetric Determination of Sulfates by Oxidation of Benzidine Sulfate with Potassium Permanganate," Soil Sci., 8:61-65 (1919).

Titration with $KMnO_4$; discussion.

119. Honda, M., "Ion-Exchange Resins in Analytical Chemistry. XIV. Determination of Sulfate Ion with Ion-Exchange Resins," Japan Analyst, 2:451-455 (1953).

Two methods using ion exchangers followed by titration with NaOH and $AgNO_3$ or alkali hydroxide.

120. Iokhelison, D. B., "Colorimetric Method for Determination of Sulfuric Acid in Drinking Waters," Ukrain Khein. Zhur, 9:25 (1934).

$SO_4^=$ to $PbSO_4$ in NaOH solution via $Pb(NO_3)_2$ precipitate and Na_2S for comparison with standard.

121. Iolson, L. M., "Application of the Volumetric Method of A. V. Vinogradov to the Determination of the Sulfate Ion in Common Salt and Pickling Baths," Zavodskaya Lab., (10):27-28 (1933).

Precipitation of $BaSO_4$ with $BaCl_2$; titration with $K_2Cr_2O_4$ with rosolic acid as indicator; hot solution must be used.

122. Iritani, N., "Determination of Sulfate Ion with EDTA. II. Chelometric Determination of Sulfate Ion as Lead Sulfate," Bunseki Kagaka, 8:30-33 (1959).

$Pb(NO_3)_2$. Excess Pb titrated using EDTA with Cu-PAN indicator.

123. Iritani, N., "Determination of Sulfate Ions with EDTA. III. Determination of Phosphate and Sulfate Ions as Magnesium Ammonium Phosphate and Lead Sulfate," Bunseki Kagaku, 9(1):1-5 (1960).

Discussion of effect of nitrate; excess Pb titrated with EDTA.

124. Iritani, N., "Volumetric Analysis of Sulfate Ion with Barium Ethylenediaminetetraacetate," Bunseki Kagaku, 7:42-46 (1958).

EDTA precipitation; excess EDTA titrated with $BaCl_2$ and EtOH with metal phthalein as indicator; if salt content high, titrate with $MgCl_2$ with Eriochrome Black T indicator.

125. Iwasaki, I., "Colorimetric Determination of a Trace of Sulphate Ion," J. Chem. Soc. Japan, Pure Chem. Sect., 74:400-401 (1953).

Determination by diphenylcarbazide.

126. Iyer, M. P. V., "Adsorption Indicator in the Volumetric Estimation of Sulfates," J. Indian Chem. Soc., 12:164-167 (1935).

Fluorescein as an indicator with Ba^{++} titration.

127. Jangida, B. L., "Microtitrimetric Determination of Sulfate in Thorium Nitrate and Reagent Chemicals," Indian J. Chem., 2(4):149-151 (1964).

$SO_4^{=}$ + $Pb(NO_3)_2$ in Me_2CO, EtOH and HOAc, and centrifuged. Dissolved in buffer and excess EDTA; titrated with $MgCl_2$ and Eriochrome Black T. Sample cleaned up with Al_2O_3. Cl^-, F^-, $CrO_4^{=}$, and PO_4^{3-} interfere. Cl^- and F^- eliminated by heating to fumes with $HClO_4$. $CrO_4^{=}$ removed by reducing with H_2O_2 and complexing with HOAc. Zn added before Al_2O_3 removed PO_4^{3-}.

128. Jarkim, A. F. S., "Volumetric Determination of Sulfates," *Rev. Soc. Bra-Sil. Quim*, 10:104-108 (1941).

Precipitation with Ba. Excess precipitated with $(NH_4)_2C_2O_4$. Oxalic acid titrated with $KMnO_4$.

129. Jaselskis, B., "Titrimetric Determination of Semimicro Amounts of Sulfate in Presence of Phosphate," *Anal. Chem.*, 36(10):1965-1967 (1964).

Titration with $Ba(IO_3)_2$.

130. Jellinek, K., "Hydrolytic Precision Analyses. Determination of Barium, Lead and Sulfate," *Z. Anorg. Allgem. Chem.*, 130:253-262 (1923).

Titration with K_2CrO_4 with methyl red as indicator; need excess Ba^{++}.

131. Jellinek, K., "Some New Methods of Volumetric Analytical Determination of Sulfate, Lead, Acid and Ammonia," *Z. Anorg. Allgem. Chem.*, 124:185-202 (1922).

Precipitation with $Ba(NO_3)_2$ followed by excess of K_2CrO_4. Back titration with $Ba(NO_3)_2$.

132. Josephson, B., "Volumetric Method for the Determination of Sulfur and Sulfate Ion," *Analyst*, 64:181-185 (1939).

Added excess $BaCl_2$ and dilute HCl; add NaOAc, HOAc and K_2CrO_4; filter; determine excess $CrO_4^=$ iodometrically.

133. Jones, J. H., "Semimicro Method for the Determination of Sulfur in Organic Substances," *J. Assoc. Official Agr. Chem.*, 26:182-186 (1943).

S oxidized to $SO_4^=$ by HNO_3, HCl, $HClO_4$; $SO_4^=$ titrated with $BaCl_2$ in presence ot tetrahydroxyquinone indicator; end point observed in presence of AgCl.

134. Kahler, H. L., "Determination of Sulfate by the Tetrahydroxyquinone Method. Effect of Sodium Sulfite and Procedure for Its Elimination," *Ind. Eng. Chem., Anal. Ed.*, 12:266-267 (1940).

Discussion.

135. Kahn, B. S., "Colorimetric Determination of Inorganic Sulfate in Small Amounts of Urine," J. Biol. Chem., 80:623-629 (1928).

Add benzidine, filter, and diazotize precipitate with PhOH to produce yellow color.

136. Kainzner, A., "Determination of Sulfate with Complexon," Zement-Kalk-Gips, 10:281-283 (1957).

Precipitation with Ba and titration with complexon (MTB).

137. Klinke, K., "The Volumetric Determination of Sulfate in Very Small Quantities," Biochem. Z., 154:171-175 (1924).

Addition of K_2CrO_4 and $BaCl_2$. Filter, add KI, titrate with $Na_2S_2O_3$.

138. Kochor, S. J., "Detection of Barium, Sulfur, and Sulfates," Ind. Eng. Chem., Anal. Ed., 9:331 (1937).

$BaCl_2$ titration. Spot test for end point.

139. Kochor, S. J., "Determination of Barium, Sulfur and Sulfates. A Rapid and Accurate Volumetric Method," Ind. Eng. Chem., Anal. Ed., 9:288-290 (1937).

Spot reaction with hydroxybenzoquinone derivative.

140. Kolthoff, I. M., "The Determination of Sulfate by Means of Barium Chromate Suspensions," Rec. Trav. Chim., 40:686-689 (1921).

$BaSO_4$ titration; excess CrO_4 titrated iodometrically.

141. Körbl, J., "Some New Metallochromic Indicators of the Complexone Type," Chem. and Ind., pp. 233-234 (1957).

Discussion of compounds for complexometric titrations.

142. Koszegi, D., "New Analytical Determination of the Sulfate Ion," Z. anal. Chem., 77:203-209 (1929).

Modification of chromate method.

143. Kotik, F. I., "Rapid Analysis of Sulfates in an Ethylenediamine Electrolyte for Copper Plating with the Nitchromazo Indicator," Zavodsk. Lab., 34(1):33 (1968).

Titrate with $BaCl_2$ in 50% EtOH with nitchromazo indicator. Used ion exchange.

144. Krausz, I., "Titrimetric Determination of Sulfate Ions," Magyar Kém. Folyóirat, 78(10):502-503 (1972).

Precipitation with benzidine sulfate and NaOH. Titrate with HCl.

145. Kuznetsov, V. I., "Metal Indicator for Barium in Volumetric Sulfate Determination in the Presence of Phosphates and Arsenates," Zavodsk. Lab., 31(5):538-540 (1965).

Ba salt titration of $SO_4^=$ using Nitchromazo as indicator.

146. Kyte, V., "An Inexpensive High-Frequency Titration Apparatus for General Laboratory Use. Application to Some EDTA and Precipitation Titrations," Analyst, 84:647-654 (1959).

Description and use in $SO_4^=$ precipitation titration.

147. Lakomkin, I. G., "Oxalate Method of Determining Sulfate Ion," Zavodsk. Lab., 8:416-421 (1939).

0.5 mg/ml determined by adding Na_2CO_3 and filtering. Neutralized with HCl; add BaC_2O_4 and filter. Acidify and titrate with $KMnO_4$.

148. Lang, K., "A Colorimetric Microchemical Method for Determination of Sulfur and Sulfate in Biological Fluids," Biochem. Z., 213:469 (1929).

Excess $BaCrO_4$ determined with phenylcarbazide.

149. Lang, W. R., "An Improved Form of Apparatus for the Rapid Estimation of Sulfates and Salts of Barium," J. Chem. Soc., 92:1370-1373 (1907).

Titration with $BaCl_2$.

150. Lederc, R., "Volumetric Determination of Sulfate," Mém. Services Chim. état, 32:15-19 (1945).

Precipitation of $PbSO_4$ and titration of excess Pb^{++} with $(NH_4)_2MoO_4$.

151. Lee, S. W., "Volumetric Determination of Sulfates. Tetrahydroxyquinone as an External Indicator," Ind. Eng. Chem., Anal. Ed., 14:839-840 (1942).

$SO_4^=$ titrated with $BaCl_2$; transferred to spot of Na salt of tetrahydroxyquinone; yellow to pink color change; acid, NaCl and Al interfere.

152. Légradi, L., "Titrimetric Determination of Sulfate Ions," *Magyar Kém. Folyóirat*, **64**:29-30 (1958).

Add $BaCl_2$. Titrate with Complexon II (analogue of MTB).

153. Leithe, W., "Oxidimetric Titration of Extremely Small Quantities of Sulfate," *Mikrochemie ver. Mikrochim. Acta*, **33**:173-183 (1947).

Excess $CrO_4^=$ titrated with standard $FeSO_4$ with diphenylaminesulfonic acid with modifications for various amounts of SO_4.

154. Li, L., "Complexometric Titration of Sulfate Ion," *K'o Hsuch T'ung Pao*, **1**:33-34 (1962).

Indirect from $PbSO_4$ precipitate-Pb titration with EDTA, xylenol orange indicator.

155. Lovasi, J., "Rapid Determination of Sulfate in Solutions Used in Uranium Production," *Kohasz, Lapok*, **8**(10):477-479 (1965).

Titration with $BaCl_2$ with Na alizarin indicator.

156. Luchinskii, G. P., "Iodometric Determination of the Sulfate Ion," *Zavodskaya Lab.*, **10**:263-265 (1941).

BaS_2O_3 precipitation; excess BaS_2O_3 titrated with iodine solution.

157. Lukin, A. M., "Detection of Sulfur in Organic Compounds," *Metody anal. Khim. Reaktiv Prep.*, **18**:151-152 (1971).

Titration with $Ba(NO_3)_2$ using chlorophosphonazo II indicator.

158. Lukin, A. M., "Titrimetric Determination of Sulfates with Chlorophosphonazo III," *Zavodsk. Lab.*, **34**(9):1054-1056 (1968).

$SO_4^=$ detected by titration in 80% acetone of pH 1 to 3 with Ba salt solution in presence of chlorophosphonazo III indicator; Ca and Sr interfere.

159. Macchia, O., "The Volumetric Estimation of Sulfate Ion," *L'Industria Chimica*, **4**:480-483 (1929).

Treatment with $Ba_3(PO_4)_2$ and NaOH. Titrate with HCl.

160. MacNevin, W. M., "An Ion-Exchange Experiment for Quantitative Analysis," *J. Chem. Education*, **28**:389-390 (1951).

Student exercise. Ion exchange $SO_4^=$ to H_2SO_4. NaOH titration.

161. Mahoney, J. F., "Improved Semimicrodetermination of Sulfur in Organic Materials. Peroxide-Carbon Fusion Followed by a Titration Using Tetrahydroxyquinone Indicator," *Ind. Eng. Chem., Anal. Ed.*, **14**:97-98 (1942).

S oxidized to inorganic $SO_4^=$ by Na_2O_2-C fusion; $SO_4^=$ determined by titration with standard $BaCl_2$ solution.

162. Manov, G. G., "Determination of the Sulfate Ion. The Microvolumetric Chromate Method," *Ind. Eng. Chem., Anal. Ed.*, **9**:198-200 (1937).

$BaSO_4$ precipitated in $HClO_4$ with carbonate-free NH_3 solution to lessen danger of co-precipitation of $CrO_4^=$ with $BaSO_4^=$.

163. Markova, L. V., "Stilbnaphthazo as an Indicator in the Volumetric Determination of Sulfate," *Ukrain. Khim. Zhur.*, **23**:89-91 (1957).

Indicator for $BaCl_2$ titration. Me_2CO or iso-AmOH added to titration mixture.

164. Marsden, A. W., "Benzidine Method for the Micro-Determination of Sulfate--Application to the Determination of Total Sulfur in Soil Solutions, Extracts, Etc.," *J. Soc. Chem. Ind.*, **56**:464 (1937).

Precipitation of $SO_4^=$ and eventual titration of benzidine with $KMnO_4$.

165. Matsui, S., "Rapid Procedure for Determination of Sulfate in Sodium Chloride Brine for Electrolysis," *Kôgyô Kagaku Zasshi*, **59**:591-592 (1956).

EDTA indicator with EBT and methyl red to improve sharpness.

166. McCallum, J. R., "Analysis for Small Amounts of Calcium, Magnesium, Barium, and Sulfate with Phthalein Purple," *Can. J. Chem.*, **34**:921-925 (1956).

$BaCl_2$ precipitation; back titrate with EDTA; phthalein purple, methyl red, and Dianil Green indicator mixture.

167. McKittrick, D. S., "Determination of Sulfate by the Benzidine Method," *Arch. Biochem.*, **6**:411-417 (1945).

Benzidine SO_4 precipitated at pH 2.8, washed and titrated with hot NaOH (phenol red).

168. Medinskii, K. L. B., "Examination of the Mindalev Method for the Volumetric Determination of Sulfates," Zavodskaya Lab., 3:230-231 (1934).

Titration with $Pb(NO_3)_2$ in presence of KI.

169. Mehlig, J. P., "Ceriometric Method for the Determination of Sulfates," Chemist Analyst, 30:76-78 (1941).

Treat with BaC_2O_4. Titrate with ceric ammonium sulfate.

170. Menis, O., "Automatic Spectrophotometric Titration of Fluoride, Sulfate, Uranium, and Thorium," Anal. Chem., 30(11):1772-1776 (1958).

High sensitivity by titration in 50% isoamyl alcohol--barium perchlorate/thorin; 520 mμ.

171. Milner, O. I., "Titration of Sulfates with Aid of a High-Frequency Oscillator," Anal. Chem., 24(8):1247-1249 (1952).

0.1 to 7.0 mg $SO_4^{=}$. 18.5 μH; titrate with $BaCl_2$.

172. Mirdalev, Z., "A New Titrimetric Determination of the Sulfate Ion," Z. anal. Chem., 75:392-395 (1928).

$Pb(NO_3)_2$ + KI.

173. Mitler, C. C., "Volumetric Determination of Small Quantities of Barium and Sulfate with Barium Rhodizonate as an Indicator--Determination of Sulfur in Iron Pyrites," J. Chem. Soc., pp. 401-406 (1940).

$SO_4^{=}$ determined using Ba rhodizonate in absolute EtOH.

174. Morgulis, S., "An Iodometric Method for Determination of Sulfates in Organic Material," Biochem. Z., 249:409 (1932).

Excess $BaCrO_4$ to H_2CrO_4. Add KI and titrate with $Na_2S_2O_3$.

175. Morris, A. G. C., "Dissolution of Barium Sulfate by EDTA and Sodium Hydroxide," Chemist Analyst, 48:76,84 (1959).

Ba precipitation; EDTA titration.

176. Mukai, K., "Simple Determination of Sulfate by Means of Dissolving Barium Sulfate with Ethylenediaminetetraacetic Acid (EDTA)," *Bunseki Kagaku*, **6**:732-735 (1957).

Precipitate $BaSO_4$ with $BaCl_2$; filter; wash; add EDTA, aqueous NH_3 to pH 11; boil; titrate unreacted EDTA with metal phthalein indicator. Cations do not interfere.

177. Mukoyama, T., "Rapid Determination of Sulfate. Titration of Ammonium, Sodium, and Potassium Sulfate by Use of Sodium Rhodizonate Test Paper," *Japan Analyst*, **4**:558-563 (1955).

Titrate using $BaCl_2$ precipitation and Na rhodizonate test paper as external indicator.

178. Munger, J. E., "Volumetric Determination of Sulfate Ion by Using Barium Ion and a Standard Disodium Dihydrogen Ethylenediaminetetraacetate Solution," *Anal. Chem.*, **22**(10):1455-1457 (1950).

Determination of excess Ba with Eriochrome Black T as indicator.

179. Murakami, T., "A Rapid Determination of Sulfate in Cellulose Acetate," *Kôgakuin Daigaku Kenkyû Hôkoku*, **7**:47-51 (1959).

Iodometric titration of excess $CrO_4^=$; 0.02% $SO_4^=$ lower limit.

180. Musha, S., "Application of High-Frequency Titration," *Science Repts. Res. Inst. Tohoku Univ. Ser. A*, **4**:575-581 (1952).

HF titration of $SO_4^=$ with $BaCl_2$; 40 to 50% MeOH at 6.0 pH.

181. Mutschin, A., "Indirect Titration of Sulfate with Barium Chloride with Sodium Rhodizonate as Indicator," *Z. anal. Chem.*, **108**:309-316 (1937).

Determination of $SO_4^=$ in presence of various interferents studied; $BaCl_2$ precipitation.

182. Mutschin, A., "Indirect Titration of Sulfate with Barium Chloride with Sodium Rhodizonate (or the sodium salt of tetrahydroxyquinone) as Internal Indicator. I," *Z. anal. Chem.*, **108**:8-18 (1937).

General discussion.

183. Nakata, H., "Volumetric Determination of Sulfate by the Use of Sodium Palmitate," *Japan Analyst*, **4**:621-623 (1955).

Titration with H_2SO_4-EtOH solution.

184. Nastaskina, E. I., "Determination of Sulfates by the Drop Method," *Elek. Stantsii*, **27**(9):55-56 (1956).

Titration with $BaCl_2$; disodium rhodizonate as indicator.

185. Nastaskina, E. I., "Volumetric Determination of Sulfates in Water," USSR Patent 102,780, 25 May 1956.

$SO_4^=$ precipitated with excess $BaCl_2$; excess Ba titrated with Na_2SO_4 with disodium rhodizonate as indicator.

186. Nazarenko, V. A., "Titration of Barium Salts and Sulfate Ion with Potassium Chromate," *Zavodskaya Lab.*, **4**:515-518 (1935).

Titration of excess $BaCl_2$ with K_2CrO_4 in presence of rosolic acid with EtOH.

187. Nechiporenko, A. P., "Microspectrophotometric Titration of Cadmium and Sulfate Ion," *Zavodsk. Lab.*, **35**(4):432-433 (1969).

$BaCl_2$ titration with nitchchromazo indicator at 664 mμ. One to 20 μg/ml; ± 0.1 to 3%.

188. Nechiporenko, G. N., "Determination of Sulfate Ions by Direct Titration with Lead Nitrate and Dithizone as an Indicator," *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk.*, pp. 359-361 (1958).

0.5 to 50 mg $SO_4^=$ detected if Cl not more than 7x $SO_4^=$, and Ca^{++} not more than 1/3x $SO_4^=$, ± 1 to 2%.

189. Neehamkin, H., "Determination of Soluble Sulfate," *Chemist Analyst*, **41**:31-33 (1952).

$SO_4^=$ solution passed through BaC_2O_4; $C_2O_4^=$ titrated with .1 N $KMnO_4$; 0.13 to 0.31 g SO_4 detected, ± 0.3%.

190. Niwa, U., "Photometric Endpoint in the Precipitation Titration of Sulfate," *Chemist Analyst*, **49**:102-103,105 (1960).

Titration with $Pb(NO_3)_2$ in acetone-water with dithiazone indicator.

191. Nonova, D., "Complexometric Determination of Barium," *Fresenius Z. Anal. Chem.*, **265**(1):31 (1973).

Cu(II)-EDTA-PAR as indicator (see Puschel).

192. Odler, I., "Complexometric Determination of Sulfates," *Chem. Zuesti*, **15**:563-567 (1961).

Indirect $PbSO_4$ titration using Complexone III, xylenol orange indicator.

193. Ogg. C. L., "Volumetric Determination of Small Amounts of Soluble Sulfates," *Anal. Chem.*, **20**(1):83-85 (1948).

Titration $BaCl_2$. Indicator: dipotassium rhodizonate or tetrahydroxyquinone.

194. Oosting, M., "Some Experiences with High-Frequency Titrations," *Chem. Weekblad*, **52**:665-670 (1956).

Pro-con discussion, construction details. $SO_4^=$ titration in boric acid medium.

195. Palatý, V., "Determination of Sulfate," Chem. Ind., p. 176 (1960).

Colorimetric determination of $SO_4^=$ using Pyrocatechol Violet, SPADNS, Eriochromecyanine R, and Alizarin Red S dyes possible; Methylthymol Blue and Thorin not suitable.

196. Peabody, W. A., "Sulfate Titration. Use of Tetrahydroxyquinone in a Semimicromethod," *Ind. Eng. Chem., Anal. Ed.*, **10**:651-652 (1938).

$BaCl_2$ precipitation with tetrahydroxyquinone and 2-methoxyethanol as an external indicator on a spot plate.

197. Philipp, B., "The Complexometric Sulfate Determination with Phthalein Complexon," *Faserforsch. u. Textiltech.*, **7**:525-527 (1956).

Comparison of gravimetric and determination with Erio T and phthalein complexon (MTB).

198. Photiadis, P., "Determination of Sulfate Ions," *Z. anal. Chem.*, **91**:173-180 (1932).

Precipitating $SO_4^=$ with $BaCl_2$; precipitating Ba with $(NH_4)_2Cr_2O_7$; titrating chromate with $Na_2S_2O_3$.

199. Polgár, E., "Rapid Titrimetric Determination of Sulfate Ions with Barium Chloride as a Measuring Solution," *Magyar Kém. Folyóirat*, **61**:48-50 (1955).

Neutralize solution and titrate to alkaline using $BaCl_2$.

200. Polushin, D., "Volumetric Determination of Sulfates," Iskussivennoe Volokno, 5(2):33-34 (1934).

Add $Pb(NO_3)_2$. Titrate excess with Na_2CO_3.

201. Ponomareva, L. K., "Rapid Determination of Sulfate in Cryolite," Tr. Ural'sk. Nauchn.-Issled. Khim. Inst., (11):54-58 (1964).

$Al(NO_3)_3$ + EtOH added to sample; titrate with $BaCl_2 \cdot 2H_2O$ with Na rhodizonate as indicator.

202. Puschel, R., "Metal Specific Indicators in Precipitation Titrations. IV. Rapid Determination of Sulfate by Titration with Standard Lead Solution," Z. anal. Chem., 166:401-406 (1959).

$SO_4^{=}$ titration with Pb solution in 50% iso-PrOH at pH 6 with 4-(2-pyridylazo)resorcinol (PAR) indicator or at pH 4 using dithizone; 2 to 100 mg $SO_4^{=}$.

203. Raeder, M. G., "Microtitrimetric Determination of Sulfuric Acid and Sulfates with Sodium Rhodizonate as Indicator," Kgl. Norske Videnskab. Selskab Forh., 5(8):32-35 (1933).

Titration with $BaCl_2$.

204. Randall, M., "Rapid Volumetric Method for the Determination of the Sulfate Ion," Ind. Eng. Chem., Anal. Ed., 14:620-621 (1942).

Sulfate + $BaCl_2$. Titrate with Na_2HPO_4, methyl red indicator.

205. Rao, G. V., "Estimation of Carboxyl, Sulfate, and Sulfonate Groups by Direct Titrimetry," Indian J. Chem., 5(4):150-152 (1967).

Titration with alcohol-KOH to determine acidity; hydrolysis with H_2SO_4, isolation of fatty acid, weighed and titrated to determine combined carboxyl and sulfonate.

206. Raschig, F., "Determination of Sulfuric Acid in Drinking Water By Means of Benzidine," Z. Angew. Chem., 40:864 (1927).

5-liter sample evaporated to 500 cc + 25 cc conc. benzidine. Filter and titrate precipitate with 0.1 NaOH.

207. Rayner, A. C., "A Rapid Titrimetric Method for Sulfate in Lead Dioxide Exposed to Atmospheric Sulfur Pollution," *J. Air Polln. Control Assoc.*, **16**(8):418-421 (1966).

Formation of ammonium sulfate and titration with $Ba(ClO)_4$ with Thorin indicator.

208. Reitmeir, R. F., "Semimicroanalysis of Saline Soil Solutions," *Ind. Eng. Chem., Anal. Ed.*, **15**:393 (1943).

Benzidine sulfate precipitate titrated with standard base. Indicator: phenol red.

209. Repiton, E., "Titrimetric Determination of Free Sulfuric Acid and Sulfate," *Mon. Sci.*, **24**:382-384

Sulfate + $BaCl_2$ + $K_2Cr_2O_7$. Excess $K_2Cr_2O_7$ titrated against $SnCl_2$. $HgCl_2$ indicator.

210. Ricci, J. E., "Determination of Sulfate. Attempt to Determine Sulfate by Titration with Lead Nitrate with Eosin as Indicator," *Ind. Eng. Chem., Anal. Ed.*, **8**:130-132 (1936).

Titration with $Pb(NO_3)_2$; ± 0.5 mg Na_2SO_4.

211. Ringbom, W., "Photometric Precipitation Titration Determination," *Z. anal. Chem.*, **122**:263-279 (1941).

Discussion of factors affecting accuracy of using $BaSO_4$ as example.

212. Riva, B., "Indirect Volumetric Determination of the Sulfate Ion with Ethylenediaminetetraacetic Acid," *Ann. Chim.*, **47**:233-239 (1957).

Eriochrome Black T indicator with Mg^{++}.

213. Rivett, A. C. D., "A Method for the Volumetric Estimation of Sulfates," *Chem. News*, **118**:253-254 (1919).

Sulfate + BaC_2O_4. Titrate with $KMnO_4$.

214. Robbin, L. A., "Rapid Titrimetric Determination of Sulfate in Mixtures of Gypsum Anhydrite, Calcium Oxide, and Calcium Sulfide Using Ion Exchange," *Anal. Chem.*, **36**(2):429 (1964).

Titration using Dowex 50 or Amberlite IR 120. Sulfate titrated as H_2SO_4.

215. Roemer, H., "Titrimetric Determination of Combined Sulfuric Acid by the Barium Chromate Method," Z. anal. Chem., 49:490-492

$SO_4^=$ exchanged via $BaCl_2$ and $K_2Cr_2O_7$ with K_2CrO_4; K_2CrO_4 titrated with standard $FeSO_4(NH_4)_2SO_4$ using K_3FeCN_6 as indicator; down to 0.1% $SO_4^=$ with 0.035 to 0.048% error.

216. Roth, H., "A New Rapid Method for the Technical Determination of SO_4 in Sulfates," Z. Angew. Chem., 39:1599-1600,1601 (1926).

Sulfate + $BaCl_2$. Titration with K_2CrO_4. pp'-diaminodiphenylamine indicator.

217. Rumler, F., "Complexometric Sulfate Determination," Z. anal. Chem., 166:23-24 (1959).

Indirect Ba titration with EDTA.

218. Ryazanov, B. A., "Volumetric Determination of Sulfate Ion," Nauch. Trudy Moskov Tekhnol, Inst. Legkoi Prom, (16):62-65 (1960).

Titration of $SO_4^=$ as $CU_2(SO_4)_3$ or $Al_2(SO_4)_3$ with $Pb(NO_3)_2$ with dithizone indicator.

219. Schoch, E. P., "Direct Titrimetric Methods for Magnesium, Calcium, and Sulfate Ions and their Applicability to Water Analysis," Ind. Eng. Chem., 19:112-115 (1927).

Add $BaCl_2$, titrate with Na_2CO_3 solution. Thymolphthalein indicator.

220. Scholle, S., "Determination of Errors at Successive Titrations of Phosphate and Sulfate Solutions," Vys, Sk. Chem.--Technol., Pardubioe, Gech. Collect Czech. Chem. Commun., 37(9):3029-3033 (1972).

Modification of Bakacz-Polgar and Szekeres method.

221. Schroeder, W. C., "Direct Titration of Sulfate: Tetrahydroxyquinone as an Internal Indicator," Ind. Eng. Chem., Anal. Ed., 5:403-406 (1933).

Titration with $BaCl_2$. EtOH and KCl used; 2 to 20 mg $SO_4^=$.

222. Seidman, E. B., "Determination of Sulfur Oxides in Stack Gases," Anal. Chem., 30:1680-1682 (1958).

Ba-thorin titration of SO_3.

223. Serfass, E. J., "Analytical Determination of Trace Constituents in Metal Finishing Effluents. XIII. The Volumetric Determination of Sulfate in Effluents," Plating, 43:500-501 (1956).

Sample precipitated with OH^- and Ag^+ to remove interferents; F^- removed by evaporation with HCl; organics oxidized with H_2O_2; $SO_4^=$ titrated with $BaCl_2$, tetrahydroxyquinone as indicator; 5 to 50 ppm range.

224. Shcherbachev, K. D., "Rapid Determination of Sulfates in Crude Hydrochloric Acid," Zavodskaya Lab., 3:424-425 (1934).

Spot titration with $K_2Cr_2O_7$ and p-aminodimethylaniline sulfate or leucomethylene blue indicators.

225. Sheen, R. T., "Determination of Sulfur in Oil. Tetrahydroxyquinone as an Indicator in Direct Titration," Ind. Eng. Chem., Anal. Ed., 10:206-207 (1938).

S in oil determined after oxidation in bomb by titration with tetrahydroxyquinone dispersed in organic medium as internal indicator.

226. Sheen, R. T., "Determination of Sulfur in Rubber. Uses of Tetrahydroxyquinone as a Titration Indicator," Ind. Eng. Chem., Anal. Ed., 9:69-71 (1937).

S oxidized to $SO_4^=$; $SO_4^=$ precipitated by excess $BaCl_2$; heavy metals precipitated by KOH at pH 8.3; excess Ba determined by back titration with Na_2SO_4 using tetrahydroxyquinone as indicator.

227. Sheen, R. T., "Direct Titration of Sulfates. Tetrahydroxyquinone as an Internal Indicator," Ind. Eng. Chem., Anal. Ed., 8:127-130 (1936).

Method of Schroeder but using iso-ProOH; $PO_4^{\equiv}$ liberated by using pH 4 by aid of bromcresol green indicator; $BaCl_2$ titrated with tetrahydroxyquinone; 80 to 3,000 ppm $SO_4^=$.

228. Shinkai, S., "New Volumetric Determination of Sulfate Ion," Japan Analyst, 2:432-433 (1953).

Sulfate + $BaCl_2$, add Na_2CO_3; add HCl, back titrate with NaOH.

229. Shpilev, F. S., "Determination of Sulfate Ion in Water-Soluble Sulfates," Trudy Dagestan. Sovef. Inst., 7:106-118 (1955).

Iodometric titration in buffer solution.

230. Shub, M. E., "Volumetric Determination of Sulfates," *Farmatsiya*, **4**(11/12):17-19 (1941).

An improvement of Raschig (benzidine $SO_4^=$) method.

231. Siegfriedt, R. K., "Determination of Sulfur After Combustion in a Small Oxygen Bomb. Rapid Titrimetric Method," *Anal. Chem.*, **23**: 1008-1011 (1951).

S oxidized, treated, and titrated with $BaCl_2$ using tetrahydroxyquinone as indicator using orange light filter; corrections can be made for Ba and P.

232. Sijderius, R., "Titrimetric Determination of Sulfate by Means of the Disodium Salt of EDTA," *Anal. Chim. Acta*, **11**:28-32 (1954).

Sulfate + $BaCl_2$. Titration with EDTA.

233. Skvortzov, V. N., "Volumetric Determination of Sulfate and Barium Ions," *Trans. Butleroy Inst. Chem. Tech. Kazan*, (1):164-167 (1934).

Titration with $BaCl_2$ in a buffered solution containing chromate.

234. Smith, J. L. B., "Volumetric Determination of Barium and Sulfate," *S. African J. Sci.*, **16**:174-176 (1919).

Sulfate + $BaCl_2$. Add K_2CrO_4; add I_2; titrate with $Na_2S_2O_3$.

235. Snyder, S., "Volumetric Determination of Sulfates by the Use of Benzidine Solution," *Chemist Analyst*, **20**(6):8-10 (1931).

Raschig's method.

236. Soibel'man, B. I., "Semimicrodeterminations of Sulfates by the Iodate Method," *Zhur. Anal. Khim.*, **3**:258-263 (1948).

Precipitation of $SO_4^=$ with $Ba(IO_3)_2$ followed by titration with $Na_2S_2O_3$ (methyl orange indicator); IO_3^- concentration ~ .1 N; if $SO_4^= \leq 0.05\%$, add known amount K_2SO_4.

237. Sonenberg, F. K. M., "Long Chain Alkyl Sulfates," *Anal. Chem.*, **22**: 175 (1950).

Complex dye rosaniline HCl extraction via $CHCl_3$ and EtAct. Application to alkyl sulfates and other strong organic acids.

238. Spiridorova, S. I., "Rapid Determination of the Concentration of Solutions of Electrolytes by Titration with Water in the Presence of Indicators of Turbidity," *Izvest. Uysshikh Ucheb. Zavedenic; Khim. i Khim. Tekhnol.*, (2):51-57 (1958).

Samples titrated with water using 50/50 iso-BuOH and EtOH indicator.

239. Sporek, K. F., "Complexometric Determination of Sulfate," *Anal. Chem.*, **30**(6):1032-1035 (1958).

Complexometric Determination of $SO_4^=$. Back titration of EDTA solution of $PbSO_4$ using $ZnCl_4$, Eriochrome Black T indicator.

240. Staikov, T., "Determination of Water-Soluble Chloride and Sulfate in Solonets Soil," *Rastenievadri Nauki*, **2**(10):113-118 (1965).

Soil extracted with $NaNO_3$, $BaCl_2$ and $Cr_2O_7^=$. Excess $Cr_2O_2^=$ titrated with $FeSO_4$. Diphenylamine indicator.

241. Strebinger, R., "New Volumetric Method for Determination of Barium and Sulfate Ions," *Z. anal. Chem.*, **79**:1-8 (1929).

Sulfate + Ba^{++}; titrate with H_2SO_4.

242. Strebinger, R., "Volumetric Determination of Sulfate with the Aid of Sodium Rhodizonate," *Z. anal. Chem.*, **105**:346-350 (1936).

Discussion.

243. Styunkel, T. B., "Determination of Sulfate by the Trilon B Method," *Zavodskaya Lab.*, **72**:653-656 (1956).

Titration with Trilon B.

244. Sümegi, L., "Determination of Sulfate Ion in Soluble Simple Sulfates," *Magyar Kém. Folyóirat*, **39**:180-181 (1933).

$SO_3^=$ precipitated with $BaCl_2$ and $(NH_4)_2CO_3$. $BaCO_3$ in precipitate titrated with HCl to methyl orange end point.

245. Sundberg, O. E., "Microdetermination of Halogens and Sulphur Using the Grote Combustion Apparatus," *Ind. Eng. Chem., Anal. Ed.*, **18**:719-723 (1946).

S determined by automatic combustion method with volumetric procedures using di-K rhodizonate as indicator.

246. Szekeres, L., "Determination of Inorganic Sulfur Compounds in the Presence of Other Ions. II. Determination of Sulfate Ions or Total Sulfur Content of Inorganic Sulfur Compounds by Precipitation Titration," *Microchem. J.*, **14**(1):63-70 (1969).

Titration with $BaCl_2$ in presence of Mg complexonate and Eriochrome Black T indicator (includes interference removal).

247. Szekeres, L., "Determination of Sulfate in Presence of Phosphate, Arsenate, and Other Ions. II," *Microchem. J.*, **13**(3):349-356 (1968).

Titration with $BaCl_2$ in presence of EDTA and DCyTA.

248. Szekeres, L., "Titrimetric Determination of Phosphate, Arsenate, and Sulfate," *Kiserl. Kozlemen A. Novenytepmesz*, **57**(3):169-172 (1964).

Titrate with $MgCl_2$ with NH_4Cl-NH_4OH buffer using Eriochrome Black T, bromopyrogallol red, or MTB as indicators.

249. Szekeres, L., "Volumetric Determination of Sulfate Ions," *Magyar Kém. Folyöirat*, **61**:298-300 (1955).

Sulfate + Na_2CO_3 + EtOH; titrate with $BaCl_2$ solution. Phenolphthalein indicator.

250. Szilagyi, M., "Indirect Acidimetric Titration of Sulfate," *Chemist Analyst*, **55**(4):109 (1966).

Sulfate + $BaCl_2$, add Na_2CO_3, titrate with HCl.

251. Talenti, M., "Volumetric Estimation of Sulfates," *Giorn. Chim. Ind. Applicata*, **8**:611-612 (1926).

Benzidine method; semi-quantitative.

252. Tanaka, T., "Determination of Sulfate with EDTA. IV. Chelatometric Determination of Sulfate as Lead Sulfate," *Bunseki Kagaku*, **8**:826-827 (1959); *Bunseki Kagaku*, **9**:1-6 (1960).

Xylenol orange indicator; 1 to 50 mg $SO_4^{=}$.

253. Tananaev, I., "Adsorption of Ions of Water by Precipitates. II," *J. Applied Chem.*, **10**:2082-2087 (1937).

Neutralize sample with NaOH to pink color with phenol red. Add 50% alcohol and titrate with $BaCl_2$. Red color increases and disappears at end point. Boil solution and titrate to end point again.

254. Tananaev, I., "Determination of Plumbous and Sulfate Ions," J. Applied Chem., 9:1725-1728 (1936).

Titration with $Pb(NO_3)_2$. "Blue ethyl acidic RR(B)," 2-(ethylaminephenylazo-1,8-dihydroxynaphthalene-3,5-disulfonic acid Na salt) indicator.

255. Tananaev, N. A., "The Volumetric Determination of Water-Soluble Sulfates," J. Chem. Ind., 8:939-949 (1931).

Sulfate + $Pb(NO_3)_2$, titrate with Na_2CO_3.

256. Thomson, M. L. "Methods for the Micro-Volumetric Determination of Sulfate," Metallurgia, 39:46-48 (1948).

Review of volumetric methods.

257. Toboleva, A. D., "New Titrimetric Process for Determining Sulfates," Energefik, 15(9):18-20 (1967).

Titration with $BaCl_2$. Nitchromazo indicator.

258. Toei, K., "Surface-Active Agents in Analytical Chemistry. I. Titrimetric Determination of Sulfate with Sulfonazo III (as an indicator)," Banseki Kagaku, 17(5):589-592 (1968).

Titration with Ba^{++}. Use of Dowfax 2A1.

259. Trandafelov, D., "Rapid Determination of Sulfate in Cryolite," Godishnik Sofiiskiya Univ., Fiz.-Mat. Fak. Kniga 2-Khim., 49:47-52 (1956).

$BaCrO_4$ titrated by iodometric method; ~ 2% error.

260. Ueno, K., "Determination of Sulfate with Ethylenediaminetetraacetic Acid (EDTA)," Japan Analyst, 3:331-332 (1954).

Determination of $SO_4^=$ with $BaCl_2$ and di-Na EDTA solution using Eriochrome Black T and $ZnCl_2 \cdot 6H_2O$, $MgCl_2 \cdot 6H_2O$, and Iodine.

261. Ueno, K., "Rapid Analysis of Viscose-Coagulating Liquor Using Schwarzenbach Method. Volumetric Determination of Zinc and Sulfate Ion," Anal. Chem., 24:1363-1364 (1952).

Free H_2SO_4 determined by titration and remaining Na_2SO_4 calculated from total $SO_4^=$ and other values.

262. Vargina, O. S., "Volumetric Determination of Sulfates," *Elek. Stantsii*, **27**(9):54-55 (1956).

Trilon B titrated with $BaCl_2$ using water hardness indicator.

263. Vernazza, E., "Rapid Volumetric Estimation of Sulfate Ions," *Industria Chimica*, **4**:988-989 (1929).

Sulfate + $BaCl_2$, add Na_2SO_4 of known concentration. Titrate back excess, congo red + 0.02 N $(NH_4)_2Cr_2O_7$ as external indicator.

264. Vinogradov, A. V., "Direct Titration of Barium Salts with Potassium Chromate in the Presence of Rosolic Acid as Indicator. Application of the Method to the Analysis of Sulfates and in Particular to the Determination of Sulfur in Pyrite and in Slags," *Ann. Chim. Anal. Chim. Appl.*, **17**:285-288 (1935).

265. Vinogradov, A. V., "Direct Titration of Barium Salts with Potassium Chromate, with Rosolic Acid as Indicator," *Zavodskaya Lab.*, (10): 17-19 (1933).

$SO_4^=$ determined by adding excess $BaCl_2$ and titrating excess Ba with K_2CrO_4 in presence of rosolic acid; Fe interferes.

266. Vinogradov, A. V., "Volumetric Determination of Sulfates with Lead Nitrate," *Zavodskaya Lab.*, **4**:167-170 (1935).

Pappenheim method (unable to obtain original document).

267. Wanninen, E., "Complexometric Determinations of Sulfate Ion with Diethylenetriaminepentaacetic acid," *Suomen Kemistilehti*, **29B**:184-188 (1956).

Add Ba salt and back titrate at pH 10 with tri-N_2 salt of EDTA in presence of Mg complex of EDTA and Eriochrome Black T.

268. Weiner, R., "Rapid Analysis of Sulfate in Chromic Acid Solutions," *Metallwaren - Ind. u. Galvano-Tech.*, **50**(2):66-70 (1959).

Reduce solution, add $BaCrO_4$, NaOAc and water. Filter, treat KI and acidify. Titrate $Na_2S_2O_3$ using starch indicator.

269. Wellings, A. W., "Direct Titration of Magnesium and Manganous Sulfates using Fluorescein as an Adsorption Indicator and the Extension of the Method to the Direct Titration of Other Soluble Sulfates and Alums," *Trans. Faraday Soc.*, **28**:561-564 (1932).

Mg or Mn $SO_4^=$ titration with $Ba(OH)_2$ using fluorescein.

270. Wenger, P. E., "Semiquantitative Determination of Sulfur Anions (sulfhydric, sulfurous, sulfuric, thiosulfuric, and persulfuric)," Helv. Chim., Acta, 32:1865-1869 (1949).

Acid, step pH titration.

271. Werner, A., "Volumetric Microdetermination of Sulfur After the Carius Decomposition of Organic Substances," Angew Chem., 52:139-140 (1939).

$SO_4^=$ by iodometric titration of chromic acid.

272. Wharton, H. W., "Application of Spectrophotometric Titrations to Micromolar Solutions of Calcium, Magnesium, Oxalate, or Sulfate," Anal. Chem., 36(8):1679-1681 (1964).

Improved end point determination (barium perchlor/thorin) 500 to 2,500 μg range.

273. White, D. C., "The Titrimetric Microdetermination of Sulfate Using Lead Nitrate as Titrant and Dithizone as Indicator," Mikrochim. Acta, pp. 254-269 (1969).

10 to 100 μg $SO_4^=$; $Pb(NO_3)_2$ titration.

274. Whiteker, R. A., "Determination of Sulfate and the Analysis of Pyrites. Application of Cation-Exchange Resins," Anal. Chem., 26(10):1602-1605 (1954).

Solution-treated ion exchange. Titrate NaOH to pH 7. Add dextrin and dichlorofluorescein and titrate to pink with $AgNO_3$.

275. Wilson, C. W., "Determination of Organic Sulfur in Gas. Titration of Sulfate in the Sulfur Lamp with Barium Chloride Using Tetrahydroxyquinone as an Indicator," Ind. Eng. Chem., Anal. Ed., 10:418-419 (1938).

SO_2 adsorbed in Na_2CO_3 in ASTM sulfur lamp; $SO_4^=$ determined directly by titrating with $BaCl_2$ solution using tetrahydroxyquinone as indicator.

276. Zabiyako, V. I., "Determim tion of Sulfate in Chromium Ammonium Alum," Tr. Ural'sk. Nauchn.-Issled. Khim. Inst., (11):49-50 (1964).

Ion-exchange to remove Cr^{+++}, etc.; alkalimetric titration of H_2SO_4.

277. Zavarov, G. V., "Some Improvements in the Direct Titration of Sulfates," *Zavodskaya Lab.*, **23**:541-542 (1957).

Titration with $BaCl_2$. Alizarin indicator.

278. Zavarov, G. V., "The Use of Sodium Rhodizonate for Determining Sulfur and Sulfates in Technical Analysis," *Zavodskaya Lab.*, **8**:993-995 (1939); *Khim. Referat. Zhur.*, (3):55 (1940).

Discussion. Na rhodizonate acceptable as external indicator.

279. Zink, J., "Determining the Sulfate Ion by the Palmitate Method," *Z. anal. Chem.*, **71**:386-387 (1927).

$SO_4^=$ and $BaCl_2$; titrate excess Ba with K palmitate; phenolphthalein end point.

CONVERSION-DETECTION

280. Archer, E. E., "Determination of Small Amounts of Sulfate by Reduction to Hydrogen Sulfide and Titration with Mercuric or Cadmium Salts with Dithizone as Indicator," Analyst, 81:181-182 (1956).

Titration with $Hg(OAc)_2$. Wet reduction, distill into dithizone.

281. Cubero, S. N., "Determination of Sulfate by Reduction to Sulfur Dioxide," Anales Real Soc. Espan. Fiz. Quim., Ser. B., 61(11):1097-1100 (1965).

$SO_4^=$ to SO_2 by powder Cu. Detected using West-Gaeke or iodometrically.

282. Davis, J. B., "Spectrophotometric Microdetermination of SO_4," Anal. Chem., 44(3):524-532 (1972).

$SO_4^=$ to H_2S by treatment with HI, Ac_2O, and Na hypophosphite. H_2S reduces Fe^{+3} and 1,10-phenanthroline to bright orange ferrous complex. Photo measured at 510 nm. Few interferences. 0-100 µg range.

283. Emery, R. St. J., "Determination of Sulfate Content of Chromium Plating Solution by Combustion Methodology," Electroplating and Metal Finishing, 13:253-257 (1960).

Reduce in O_2 stream using Fe and Sn powder. Absorb in H_2O_2 solution and titrate with NaOH to methyl red end-point.

284. Geilmann, W., "Microanalytical Determination of Sulfates," Glastech. Ber., 33:332-338 (1960).

The sulfate is reduced using HI + H_3PO_2 to H_2S, absorbed in NaOH and titrated with $CdCl_2$-dithizone indicator.

285. Gel'man, N. E., "Microdetermination of Sulfur in Organic Compounds," Zavodskaya Lab., 8:673-677 (1939).

S to H_2S using H_2 and Pt gauze; H_2S absorbed in $ZnSO_4$; S determined iodometrically.

286. Gustafsson, L., "Determination of Ultramicro Amounts of Sulphate as Methylene Blue - I. The Colour Reaction," Talanta, 4:227-235 (1960).

$SO_4^=$ as sulphide determined spectrophotometrically as methylene blue; sulphide reacts with p-aminodimethylaniline and ferric iron.

287. Gustafsson, L., "Determination of Ultramicro Amounts of Sulphate as Methylene Blue - II. The Reduction," Talanta, 4:236-243 (1960).

$SO_4^=$ reduced to sulphide by hydriodic and hypophosphorous acids in acetic acid solution.

288. Horton, A. D., "Polarographic Determination of Sulfate," Anal. Chem., 23:1859-1860 (1951).

Reduction of SO_4 to H_2S using hydriodic acid. Precipitation out as CdS. Dissolve in HCl. Determine Cd by polarography.

289. Johnson, C. M., "Microestimation of Sulfur in Plant Materials, Soils, and Irrigation Waters," Anal. Chem., 24(4):736-742 (1952).

$SO_4^=$-S reduced by mixture of HI, HCO_2H, and red P; H_2S determined spectrophotometrically with methylene blue; 1-300 μg determination limit with ± 5%.

290. Kiba, T., "Tin (II) - Strong Phosphoric Acid - A New Reagent for the Determination of Sulfate by Reduction to Hydrogen Sulfide," Bull. Chem. Soc. Japan, 28:641-644 (1955).

Tin plus concentrated $H_3PO_4 \longrightarrow H_2S$ which is titrated with iodine.

291. Larsen, R. P., "Separation and Determination of Microgram Amounts of Sulfur," Anal. Chem., 31(9):1596-1597 (1959).

Sulfur fused with vanadium pentoxide reduced over Cu; SO_2 absorbed in sodium tetrachloromercurate and determined spectrophotometrically with pararosaniline and formaldehyde.

292. Lorant, I. S., "A New Colorimetric Microchemical Method for Determination of Sulfur in Sulfides, Sulfates, Etc.," Z. Physiol Chem., 185:245-266 (1929).

Reduction of S using HI, red P and CO_2H_2; distill H_2S into $Zn(OAc)_2$ and determine using methylene blue.

293. Lorant, I. S., "A New Colorimetric Micro Method for Determination of Sulfur in Sulfides, Sulfates, Etc.," Z. Physiol Chem., 193:56-58 (1930).

Describes additional years experience. Minimum detected 0.5 μg, 5% error.

294. Luke, C. L., "Determination of Total Sulfur in Rubber," Ind. Eng. Chem., Anal. Ed., 15:602 (1943).

$SO_4 \xrightarrow{HI} H_2S$. Then iodometric titration.

295. Quartermain, P. G., "An Improved Method for Determination of Small Amounts of Sulfate," Analyst, 85:211-215 (1960).

Digest with Ti-H_3PO_4; H_2S removed with CO_2 and absorbed in NaOH solution. Titrate with $Hg(OAc)_2$ solution with diphenylthiocarbazone indicator.

296. Ramanauskas, E., "Determination of Trace Amounts of Sulphate Sulfur with Crystal Violet," Elem. Mikrokiekiu Nustatymas Fiz.-Chem. Metod., Liet. TSR Chem.-Anal. Mokslines Konf. Darb., 2nd, pp. 145-152 (1969).

Reduction with Sn and H_3PO_4 to H_2S and measure crystal violet absorption with Chloramine B and KI at 400 nm. Beers Law valid 0.161-2.08 μg/ml.

297. Rancke-Madsen, E., "Determination of Sulfate by Reduction with Stannous Chloride," Acta. Chem. Scand., 3:773-777 (1949).

Reduction with $SnCl_2$ and H_3PO_4 to H_2S, absorbed in I_2, titrate with $Na_2S_2O_3$.

298. Rancke-Madsen, E., "Determination of Sulfate by Reduction with Stannous Chloride. II," Acta. Chem. Scand., 6:305-306 (1952).

Hg, Cu interfere, Pb^{++} does not (see above).

299. Roth, H., "Colorimetric Determination of Traces of Sulfur," Mikrochemie ver. Mikrochim. Acta, 36/37:379-392 (1951).

After oxidation reduce to H_2S using HI, CO_2H_2 and hypophosphite. Collect in $Zn(OAc)_2$ and determine with methylene blue.

300. Scaringelli, F. P., "Determination of Atmospheric Concentrations of Sulfuric Acid Aerosol by Spectrophotometry, Coulometry, and Flame Photometry," Anal. Chem., 41(6):707-713 (1969).

H_2SO_4 separated from SO_2 and other sulphates. SO_3 in N_2 converted to SO_2 with hot Cu. SO_2 determined by FPD. Method can measure H_2SO_4 in presence of 100 x as much SO_2 and other sulphates.

301. Stanford Research Institute, "Size Determination of Atmospheric Sulfate and Chloride Particles," HEW Contract No. PH-86-64-54.

Thermal sulfur reduction to H_2S; determined by microcoulometric titration.

302. Stratmann, H., "Microanalytical Determination of Various Sulfur Compounds in Gases and in Solids," Mikrochim. Acta., pp. 1031-1037 (1956).

Reduction by H_2 and conversion to H_2S on a Pt catalyst. Detection by Moly Blue reaction and micro-crystal structure.

303. Volkov, I. I., "Determination of Sulfates by Reduction to Hydrogen Sulfide," Zhur. Anal. Khim., 13:686-690 (1958).

SO_4 reduced with $SnCl_2 + H_3PO_4$. $H_2S + Cd(OAc)_2 = CdS$, add to acidified I_2, titrate with $Na_2S_2O_3$.

304. Wiesenberger, E., "Microchemical Determination of Sulfur in Organic Compounds," Mikrochemie ver. Mikrochim. Acta, 29:73-86 (1941).

$S + H_2$ with Pt catalyst to H_2S and idiometric titration.

ELECTROMETRIC

305. Agasyan, P. K., "Potentiometric Determination of Lead and Sulfate Ions. I.," Vestnik Moskov. Univ., 8(5) Ser. Fiz-Mat. i Estestven. Nauk, (3):65-68 (1953).

Discusses effects of temperature, pH, etc.

306. Agasyan, P. K., "Potentiometric Determination of Lead and Sulfate Ions. II.," Vestnik Moskov. Univ., 8(8), Ser. Fiz-Mat. i Estestven. Nauk, (5):121-124 (1953).

Potentiometric titration with $K_4Fe(CN)_6$ of $SO_4^=$ solution.

307. Akhmedov, G., "Amperometric Analysis of Anion Mixtures Containing Sodium Sulfites and Thiosulfates," Nauch. Tr. Tashkent. Univ., No. 379, 3:182-188 (1970).

I_2 reduction current at rotating Pt electrode used in amperometric titration of $SO_3^=$ and $S_2O_3^=$.

308. Akimoto, N., "Potentiometric Microtitration of Sulfate Ion Using a Sodium-Selective Electrode in a Nonaqueous Medium," Anal. Chem., 46(6):766-769 (1974).

$BaCl_2$ titration.

309. Anderson, L. J., "Apparatus for Rapid Conductometric Titrations Determination of Sulfate," Anal. Chem., 19:264-268 (1947).

Conductometric titration, $BaCl_2$.

310. Atanasiu, I. A., "Potentiometric Determination of Sulfate by Indirect Titration with Benzidine," Z. anal. Chem., 90:337-340 (1932).

Excess benzidine titration with KNO_2.

311. Baudisch, J., "Direct Potentiometric Determination of Sulfate," Fresenius Z. anal. Chem., 235(3):231-234 (1968).

Titration with 10:1 mixture. .1 N Ba and Pb (NO_3). Det. delta pH. Range 100-500 mg/liter. 0.7% acc.

312. Boos, R. N., "A Volumetric Microdetermination of Organically Bound Sulfur and Organic and Inorganic Sulfates," Analyst, 84:633-635 (1959).

Sulfates + $BaCl_2$. Excess determined by potentiometric titration with Na_2EDTA. Hg ref. electrode.

313. Bruno, A., "Analysis of Wines by their Conductivities," Bull. Soc. Chim., 13:24-34 (1913).

Found conductivity measurement did not agree with precipitate results.

314. Butenko, G. A., "Polarometric Determination of Sulfate Ion," Zavodskaya Lab., 9:634-635 (1940); Kim. Referat. Zhar., 4(1):88-89 (1941).

$Pb(NO_3)_2$ titration.

315. Cassidy, N. G., "Electrometric Method for Determining Sulfate Ion," Analyst, 81:169-175 (1956).

$PbSO_4$ precipitate with $Pb(NO_3)_2$ in ETOH .Titrate excess Pb with $K_2C_rO_4$. Delta pH end point.

316. Chounyk, N. G., "Use of a Limiting Current of Lead Ions in Polarography and Amperometry," Metody Kontr. Khim. Sostava Neorg. Org. Soedin, pp. 52-58 (1966).

Rotating Pt anode; $NaNO_3$ supporting medium for $SO_4^=$ determination.

317. Christensen, B. E., "Rapid Potentiometric Method for Determination of Sulfate," Ind. Eng. Chem., Anal. Ed., 10:413-414 (1938).

$BaCl_2$ titration. Best results with 25-60 alcohol.

318. Coetzee, C. J., "Anion-Responsive Electrodes Based on Ion Association Extraction Systems," Anal. Chem., 40(13):2071 (1968).

Direct reading electrodes - $SO_4^=$, 10^{-1} to 10^{-5} M.

319. Coetzee, C. J., "Liquid-Liquid Membrane Electrodes Based on Ion-Association Extraction Systems," Anal. Chem., 41(8):1128-1130 (1969).

pH dependency and effect of interfering anions.

320. Cortellessa, G. C., "Potentiometric Microdetermination of the Sulfate Ion," Analyst, 93(1109):546-547 (1968).

Titrated with lead nitrate.

321. Davies, W. C., "Amperometric Determination of Sulfates," Ind. Chemist, 19:167-169 (1943).

Polarographic titration with $Pb(NO_3)_2$.

322. Dolgaleva, A. A., "Semiautomatic Instrument for Amperometric Titration (of Sulfates and Chlorides in Paper)," Bum. Prom., 9:15 (1967).

Soviet pulp and paper industry standard test method. No chemical details in C.A.

323. Dutoit, P., "Simultaneous Determination of Sulphates, Acidity on Tanning Substances in Wine," Schweiz Wochschs., 46:690-694 (1909).

Used pt electrode. Titrated to first break in curve with $Ba(OH)_2$.

324. Duval, R., "Differential Electrometric Titration," Compt. Rend., 205:1237-1238 (1937).

Comparative electrical measurement with bridge circuit.

325. Freak, G. A., "The Effect of Dilution in Electro-Titrimetric Analysis," J. Chem. Soc., 115:55-61 (1919).

Discussion of early methods and limitations.

326. Galkin, D. E., "Electrometric (Potentiometric) Method for the Determination of Sulfate Ions," Trudy Tomsk. Gosudarst Univ. im. V. V. Kuibysheva, Ser. Khim., 145, (5-ya) Nauch. Knof., pp. 163-172 (1954). Konf. Pub. 1957.

$SO_4^=$ determination with bi-metallic electrodes combined with $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ electrode to detect excess Pb.

327. Gardner, G. L., "Complex Formation in Lead Sulfate Solutions," Anal. Chem., 42(7):794-795 (1970).

Determined dissociation constants of $PbSO_4$.

328. Gladyshev, V. P., "Direct Oscillopolarographic Determination of Sulfates," Zavodsk. Lab., 28:1063-1065 (1962).

10^{-3} to 10^{-4} M $SO_4^=$; 7 to 8% accuracy.

329. Goldstein, G., "Conductometric Determination of Sulfate by the Nonaqueous Barium Acetate Method," Anal. Chem., 34:1169-1170 (1962).

$SO_4^=$ precipitate with BaAc in HAc. Excess BaAc determination by electrotitration with perchloric acid.

330. Goldstein, G., "Indirect Determination of Sulfate by Nonaqueous Titrimetry," Anal. Chem., 33(2):266-268 (1961).

Sulfate precipitated by barium acetate. Potentiometric titration determines the excess acetate.

331. Gordon, B. E., "Determination of Sulfite and Sulfate (as Sodium Sulfate) in Sodium Petroleum Sulfonates - An Amperometric Titration," Anal. Chem., 25:897-901 (1953).

Amperometric titration with lead ion in alcohol solution.

332. Harned, H. S., "Titration of Some Bivalent Metal Sulfates by the Conductance Method," J. Am. Chem. Soc., 39:252-266 (1917).

Titration with $Ba(OH)_2$.

333. Havas, J., "Potentiometric Determination of Sulfate by Ion Selective Membrane Electrode," Proc. Conf. Appl. Phys. Chem., 2nd Ed., 1:625-629 (1971).

Combined $SO_4^=$ electrode(PbI_2 precipitate as auxiliary material with renewable surface and iodide-selective membrane electrode) used for $SO_4^=$ determination; iodide-selective electrode also useful for $SO_4^=$ determination by determination of I^- after ion-exchange between PbI_2 and $SO_4^=$.

334. Henscheid, T., "Application of Ion-Selective Electrodes in the Beet Sugar Industry," American Soc. Sugar Beet Technol., 16(6):482-495 (1971).

Potentiometric titration of $SO_4^=$ - Beet Sugar.

335. Heyrovsky, J., "Analytical Method of Electrolysis with a Cathode of Dropping Mercury," Bull. Soc. Chem., 41:1224 (1927).

Mentioned that it would be possible to titrate $SO_4^=$ amperometrically - History.

336. Heyrovsky, J., "Bibliography of Publications Dealing with the Polarographic Method from 1940-1945," *Collection Czechoslov. Chem. Commun.*, **12**:156-192 (1947).

337. Hokhstein, Y. P., "Polarographic Determination of Sulfate Ion III.," *Zavodskaya Lab.*, **5**:1444-1447 (1936).

Ba by polarimetric titration.

338. Humphrey, R. E., "Polarographic Determination of Chloride, Cyanide, Fluoride, Sulfate and Sulfite with Metal Chloranilates," *Anal. Chem.*, **43**(13):1895-1897 (1971).

Range 10^{-3} to 10^{-5} M; linear curve (μa/ppm); Polarographic-(Me) cellulose acetic acid, Ba chloranilate.

339. Ishibashi, M., "Amperometric Titrations. III. Studies with a Short Circuited System," *Sbornik Mezinarod. Polarograf. Sjezda, Praze, 1st Congr.* Pt. I, pp. 115-116 (1951).

$SO_4^=$ by excess Pb using dropping Hg electrode. No experimental details.

340. James, H. J., "Electrode for Potentiometric Measurements," *Ger. Offen*, 2,215,378, *U.S. Appl.*, 219,119, 19 January 1972.

Patent papers.

341. James, H. J., "Coated Wire Ion Selective Electrodes," *Anal. Chem.*, **44**(4):856-857 (1972).

PVC coated Pt wire. $SO_4^=$- fast linear response - .1 to 100 m M.

342. Jamieson, G. R., "Volumetric Determination of Sulfate by Using a High-Frequency Conductimetric Method," *J. Appl. Chem.*, **7**:81-86 (1957).

NO_3 interferes, Cl does not. Ba, Pb, octa-ammino-μ-nitrocobaltic tetra nitrate and hexa-amminocobaltic bromide as precipitates, poor sensitivity (2 mg).

343. Jander, G., "Conductivity Titration with Visual Observance: A Conductometric Determination of Sulfate in a Boiling, Aqueous Solution," *Z. Angew. Chem.*, **42**:1037-1038 (1929).

Lecture on electrometric titration (1929). $SO_4^=$ as example.

344. Jasinski, R., "Application of a Sulfate-Sensitive Electrode to Natural Waters," Anal. Chem., **45**(7):1277-1279 (1973).

150 mg. $SO_4^=$/liter.

345. Jasinski, R., "Potentiometric Titration of Sulfate Using an Ion-Selective Iron Electrode," Anal. Chem., **44**(14):2373-2376 (1972).

Indirect sulphate electrode based on ferric iron/$SO_4^=$ complex. No Cl, NO_3, HCO_3 interference.

346. Johannesson, J. K., "A Note on the Determination of Low Concentrations of Sulfate in Rain and Other Waters," New Zealand J. Sci., **1**:423-424 (1958).

0-10 ppm $SO_4^=$; ion exchange $SO_4^=$ to H_2SO_4, add mercuric oxide; determine $SO_4^=$ by conductivity.

347. Keller, R. E., "Titrimetric Determination of Sulfates by Diazo Titration of Benzidine Sulfate," Anal. Chem., **26**(9):1518-1519 (1954).

$SO_4^=$ determined by presence of sulfonates by benzidine sulfate precipitation; precipitate titrated potentiometrically with KNO_2; W-calomel electrode.

348. Kling, A., "Physico-Chemical Determination of Sulfates," Compt. Rend., **158**:487-489.

Investigated Dutoit's method and found to be subject to large interferences.

349. Kokina, T. A., "Electrometric Ultramicrotitration of Sulfate Ion," Zh. Anal. Khim., **26**(11):2237-2239 (1971).

Potentiometric $Pb(NO_3)_2$ titration for trace amounts of $SO_4^=$. Total volume 3-5 µ liter.

350. Kolthoff, I. M., "Amperometric Titrations. VI. The Titration of Sulfate and Some Other Anions with Lead and the Reverse Titrations," J. Am. Chem. Soc., **62**:3332-3335 (1940).

$SO_4^=$ titration with $Pb(NO_3)_2$ using dropping Hg electrode.

351. Kolthoff, I. M., "Conductometric Titration of Sulfate and Barium," *Ind. Eng. Chem., Anal. Ed.*, **3**:129-133 (1931).

$BaCl_2$ titration alkali and $ZnSO_4$. Best results--very dilute solutions with 30% ETOH; investigations of "knickpoint" versus equivalence point deviations.

352. Kolthoff, I. M., "The Use of Conductivity Titrations in Precipitation Analyses. V. Conductivity Titrations with Barium Salt," *Z. Anal. Chem.*, **61**:433-438 (1922).

Al, Fe, Ca, and NO_3 interfere.

353. Kreshkov, A. P., "Determination of Sulfuric Acid, Bisulfates, and Sulfates," *Zavod. Lab.*, **34**(11):1295-1296 (1968).

Potentiometric titration in 2:1 Me_2CO-CH_2OHCH_2OH with KOH.

354. Lukkari, U. O., "Membrane Electrodes. I. Barium Chromate-Impregnate Silicone Rubber Membrane," *Suom. Kemistilehti B*, **45**(5-6):182-185 (1972).

May be used in precipitation titrations for $SO_4^=$.

355. Lyalikov, Y. S., "Polarimetric Method of Anion Analysis. Amperometric Titration with Lead Ions," *Zhur. Anal. Khim.*, **1**(2):147-157 (1946).

General theory review.

356. Majer, V., "Polarimetric Titrations," *Z. Elektrochem*, **42**:120-123 (1936).

Description of early polarimetric titration.

357. Mather, W. B., Jr., "Coulometric-Acidimetric Titration of Fluoride in Acetic Anhydride," *Anal. Chem.*, **33**:132-134 (1961).

Discussion; potentiometric determination of end-point.

358. Mayer, J., "Detection Limit in the Polarographic Microdetermination of Sulfates in Water," *Fortschr. Wasserchem. Ihrer Grenzgeb.*, **11**:181-188 (1969).

$SO_4^=$ replacement by CrO_4; Cr determined polarographically; compares well with gravity and titration.

359. Mayer, J., "Polarographic Microdetermination of Sulfate," *Anal. Chem.*, **39**:1460 (1967).

Polarographic method using conversion of $SO_4^=$ to CrO_4. Range 0 to 50 mg/liter.

360. Miller, A. D., "Direct Potentiometric Titration of Sulfate Ion with an Indicator Electrode $Mo(MoO_3)BaSO_4$ I.," *Zhur. Anal. Khim.*, **11**:615-620 (1956); *J. Anal. Chem.*, **11**:655-660 (1956).

Preparation of the electrode. Ba titration. Range 0.008 to 0.100 N $SO_4^=$.

361. Mohan, M. S., "Preparation and Properties of the Sulfate Ion-Selective Membrane Electrode," *Anal. Chem.*, 45(8):1323-1326 (1973).

Construction details.

362. Müller, E., "The Electrometric Determination of Soluble Sulfates," *Z. Arong. Chem.*, **133**:411-416 (1924).

$SO_4^=$ precipitated with Pb. Excess Pb determination by electrotitration with $K_4Fe(CN)_6$.

363. Mukai, S., "Potentiometric Determination of Barium, Lead, and Sulfate," *Bull. Tech. Coll. Kyasha Imp. Univ.*, **4**:17-21 (1929).

$SO_4^=$ precipitate with excess $Pb(NO_3)_2$. Excess Pb determination by potentiometric titration with K_2CrO_4.

364. Murakami, S., "Short-Circuit Amperometric Titration of Sulfate Ion," *Kobe Daigaku Kyoikugakubu Kenkyu Shuroka*, (40):11-15 (1968).

Ba at pH 5.3-7.3 using S.C.E as reference electrode and chromate indicator.

365. Myers, S. A., "Automatic Amperometric Titrations Using a Mercury Cathode," *Talanta*, **12**(2):133-138 (1965).

Apparatus described. Auto-titration of $SO_4^=$ with $Pb(NO_3)_2$ in detail. Sens. 0.001 millemole $SO_4^=$

366. Ohlweiler, A. O., "Indirect Polarographic Determination of Sulfate," *Anal. Chim. Acta*, **9**:476-488 (1953).

$SO_4^=$ by polarographic determination of Pb.

367. Pasovskaya, G. B., "Conductometric Titration of Sulfate Ions," Lab. Delo., 4(3):30-33 (1958).

Method for natural waters. Excess $BaCl_2$ titrated with Na_2SO_4. Not good for less than 12 mg/liter $SO_4^{=}$.

368. Peniston, Q. P., "Sulfite Waste Liquor Analysis," Anal. Chem., 19:332 (1947).

Conductometric. $BaCl_2$ cation exchange; Na replaces Ca; 50% IPA.

369. Pungor, E., "Membrane Electrodes in Chemical Analysis," Z. Chem., 5(1):9-14 (1965).

Permselective and reversible. $SO_4^{=}$ concentration 10^{-1}-10^{-6} M.

370. Rechnitz, G. A., "Potentiometric Measurements with Sulphate-Ion and Phosphate-Ion Sensitive Membrane Electrodes," Anal. Lett., 1(1):29-33 (1967).

Preliminary evaluation of $SO_4^{=}$-PO_4 electrodes.

371. Rechnitz, G. A., "Sulphate Ion-Selective Membrane Electrode," Anal. Chem., 44(6):1098-1099 (1972).

$SO_4^{=}$ selective crystal membrane (Ag_2S, PbS, $PbSO_4$, Co_2S).

372. Ross, J. W., Jr., "Potentiometric Titrations of Sulfate Using an Ion-Selective Lead Electrode," Anal. Chem., 41(7):967-969 (1969).

Titration of $SO_4^{=}$ with $Pb(ClO_4)_2$ with Pb-selective electrode in 50% dioxane media; Cu, Hg, Ag, PO_4, Cl, NO_3, and HCO, may interfere.

373. Salzano, F. J., "Determination of Sulfur Oxides in Gases," Ger. Offen., 2,260,193 (Cl. Goln), 14 June 1973, U.S. Appl., 206,352, 9 December 1971.

Electrochem cell for determination of SO_2, SO_3 in air. Test and Ref. electrodes in closed quartz tubes connected and filled with molten eutectic. Cell EMF was linear function of log SO_x in PPM range.

374. Saunders, A., "Specific Ion Electrode for Sulfate," HEW, U.S. 3,709,811 (Cl. 204-195M; Goln), 9 January 1973.

$BaSO_4$ in Silicone rubber membrane.

375. Selig, W., "Micro and Semimicro Determination of Sulfur in Organic Compounds by Potentiometric Titration with Lead Perchlorate," Mikrochim. Acta., 1:168-175 (1970).

Absorption in $NaNO_3$; boil, add 1,4-dioxane, titrate potentiometrically with $Pb(ClO_4)_2$ and a Pb-sensitive indicator electrode.

376. Shartukov, O. F., "Potentiometric Determination of Small Amounts of Sulfate Ions and Lead Ions," Zh. Anal. Khem., 26(10):1967-1972 (1971).

Potentiometric determination in a flow concentration cell. Range 1-200 mg/liter.

377. Sierra, F., "Potochemical Redox Indicators in Amperometry. Indirect Determinations of Anions with Disodium Dihydrogen Ethylenediaminetetraacetate," Inform. Quim. Anal., 27(2):93-98 (1973).

Thionine (I) used as photochemical redox indicator in indirect amperometric titration of $SO_4^=$.

378. Sinha, S. K., "Potentiometric Titrations with Resin Membrane Electrodes," J. Indiam Chem. Soc., 32:35-38 (1955).

Reversible resin membrane electrodes; from ion-exchange resins; used for $SO_4^=$ determination.

379. Summers, P. W., "Source and Budget of Sulfate in Precipitation from Central Alberta, Canada," J. Air Poll. Cont. Assoc., 23(3):194-199 (1973).

Precipitation samples analyzed for $SO_4^=$ by conductometric titration against barium trichloroacetate.

380. Spalenka, M., "Polarographic Studies with the Dropping Hg Electrode," Coll. Czechoslov. Chem. Commun., 11:146 (1939).

Improvement of polaragraphic titration using 33.3% ETOH.

381. Spillner, F., "Conductometric Sulfate Determination," Angew. Chem., 66:198-201 (1954).

$Ba(NO_3)_2$ - "Overtitration" is measured directly - "giving results in a 3 min period."

382. Takagi, K., "A Simple Potentiometric Method for the Rapid Determination of Sulfate," J. Electrochemical Soc., 18:123-125 (1950).

$BaCl_2$ titration with MeOH and $(NH_4)_2S_2O_8$ bi-metallic electrodes.

383. Ten'Kovtsev, V. V., "Amperometric Determination of Sulfate Ion," J. Anal. Chem., 12:523-526 (1957).

$BaCl_2/CrO_4$ double titration.

384. Tockstein, A., "Use of Complexones in Chemical Analysis. XXXIV. Polarographic Determination of Sulfates and Barium," Chem. Listy, 45:539-542 (1951); Collection Czechoslav. Chem. Communs., 16:398-404 (1951).

Indirect $SO_4^=$ determination via Ba++ interchange with Ag^+ in complex.

385. Trachtenberg, I., "Ion-Selective Electrochemical Sensors," U.S. Office Saline Water, Res. Develop. Progr. Report No. 761,(1972).

Cation sensors - Fe, Cu.

386. Ugol'nikov, N. A., "Electrometric Determination of Sulfates in Mineral Waters," Tr. Tomskogo Gos. Univ., Ser. Khim., 154:262-263 (1962).

Acidify HCl, add $K_3[Fe(CN_6)]$, $K_4[Fe(CN)_6]$ and ETOH. Titrate with $Pb(NO_3)_2$ using Pt, Ag electrode.

387. Vail, E. I., "Potentiometric Determination of Sulfate Ions," Zhur. Anal. Khim., 15:369-370 (1960).

Titration with Na_2S.

388. Visyagin, N. I., "Electrometric Determination of Soluble Sulfates," Byull. Inst. Haluigie, 12:3-11 (1939).

0.02-4% $SO_4^=$ in brine. Potentiometric titration with quinhydrone and $BaCl_2$; calomel-Pt electrodes.

389. Wagner, A., "Rapid Potentiometric Determination of Sulfate, Nitrate, and Chloride Ions in Water and Aqueous Solution," Mitt. Ver. Grosskesselbesitzer, 52:50-53 (1958).

Simultaneous SO_4, NO_3, Cl determination. Ion-ex conversion to acids. Then titration in sequence with $Ba(OH)_2$, K palmitate, and $AgNO_3$ to specified pH values.

390. West, L. E., "Vacuum-Tube Voltmeter, Application to Potentiometric Precipitation Titrates," Ind. Eng. Chem., Anal. Ed., 12:476-478 (1940).

Description of construction and use of one-tube VTVM (obsolete); $BaCl_2$ titration.

391. Woods, R., "Polarographic Kinetically Controlled Currents in Systems Containing Persulfate, Copper (II), and an Agent which Reacts with Sulfate Free Radical," Anal. Chem., 38(10):1297-1302 (1966).

Cation (Cu,As) effects on persulfate curves.

392. Young, M., "Potentiometric Determination of Sulfur Dioxide in Flue Gases with an Ion-Selective Lead Electrode," Anal. Chem., 45(13):2283-2284 (1973).

Collection in 3% H_2O_2. $SO_4^=$ precipitate with Pb. Excess H_2O_2 elimination with Zn.

393. Zando, A. M., "Electrical Conductivity as a Basis for Physiochemical Analysis," Sci. Mag. Chem. Cath., Katerinoslav, pp. 79-91 (1926).

Early work with "electrical" titration end-points. $SO_4^=$ determination - Good results only with bivalent cations.

394. Zhukov, I. I., "Potentiometric Determination of Sulfates," J. Ger. Chem., 4:962-968 (1934).

$Pb(NO_3)_2$ titration with $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ added in $ETOH/H_2O$ solution.

FLAME PHOTOMETRIC

395. Burriel, F., "Indirect Flame Photometric Determination of Sulfate Ions," Anal. Chim. Acta., 17:559-569 (1957).

$SO_4^=$ determined by precipitation with Ba^{++} or Sr^{++}; flame photo determination of cation in filtrate or centrifugate; Ba^{++} - 0 to 70 ppm $SO_4^=$; Sr^{++} - 0 to 110 ppm $SO_4^=$

396. Burriel, F., "The Indirect Flame Photometric Determination of Sulfate Ion," Rev. Cien. C. Apl., 12:16-25 (1958).

Discussion of standard curve anomalies and causes thereof.

397. Cullum, D. C., "The Flame-Photometric Determination of Barium and Sulfate - An Improved Technique," Analyst, 85:688-689 (1960).

Conversion of detergent $SO_4^=$ to Ba-NH_4 EDTA suspension.

398. Herbolsheimer, R., "Flame Photometric Determination of Sulfate," Z. anal. Chem., 20(6):418-419 (1964).

Ba emission - EDTA-triethanolamine solvent.

399. Odler, I., "Flame-Photometric Determination of Sulfates," Chem. Zvesti, 15:568-570 (1961).

$SO_4^=$ precipitated with excess $BaCl_2$ and disolved in ammoniacal EDTA. Ba determined by flame.

400. Robinson, G. A., "A Micro Method for the Determination of Sulfate by Flame Photometry," Can. J. Biochem. and Physiol., 38:643-648 (1960).

Barium emission intensified by addition of LiCl.

401. Shaw, W. M., "Indirect Flame Spectrophotometric Determination of Sulfate Sulfur," Anal. Chem., 30:1682-1689 (1958).

Ba emission with Ca, Sr, Mn interference.

FLUOROMETRIC

402. Guyon, J. C., "Fluorometric Determination of Microgram Quantities of Sulfate," Anal. Chem., 38(1):155 (1966).

Based on $SO_4^=$ interference with Thorium/Morin reaction. Simple sens. method (0 to 40 μg range). Adaptable to large numbers of samples.

403. Nasu, T. (see Spectrophotometric listing).

404. Nazarenko, V. A., "Fluorometric Determination of Sulfate Ion and Spectrophotometric Determinations of Thorium with the Help of Trihydroxyfluorene Derivatives," Zavodsk. Lab., 24:1344-1346 (1958).

Sample plus Th, detect excess Th with 9-(0-hydroxyphenyl)trihydroxyfluorone (salicylfluorone).

405. Yangsheva, V. S., "The Determination of Sulfates in Distilled Water with Salicylfluorone," Metody Anal. Kim. Reakt. Prep. Tos. Kom. Sov. Min. SSSR po Khim., 4(1962):135 (1962).

Sulfate plus $Th(NO_3)_4$ plus indicator; measure fluorescence.

GRAVIMETRIC

406. Alcino, J. F., "Microanalytical Determination of Sulfur. A Modified Bomb Method," Ind. Eng. Chem., Anal. Ed., 13:506-507 (1941).

Na_2O_2 and $KClO_3$ used; $BaSO_4$ precipitated.

407. Arrhenius, O., "Sedimetrical Methods of Analysis," Medd. Vetenskap sakad. Nobelinst., 6(14):1-69 (1926).

Quantitative estimates based on apparent volume of Ba precipitate in centrifuge tube.

408. APHA, "Gravimetric Method with Drying of Residue (156 B)," Standard Methods for the Examination of Water and Wastewater, 13th Ed., p. 333 (1971).

$SO_4^=$ gravimetric method weighing $BaSO_4$.

409. APHA, "Gravimetric Method with Ignition of Residue (156 A)," Standard Methods for the Examination of Water and Wastewater, 13th Ed., pp. 331-333 (1971).

$SO_4^=$ gravimetric method with igntion of $BaSO_4$ precipitate.

410. ASTM, "Standard Methods of Test for Sulfate Ion in Water and Wastewater (D516); Method A - Gravimetric Method," Annual Book of ASTM Standards, 31:427-428 (1974).

Details of gravimetric method using $BaCl_2$.

411. Belcher, R., "A New Reagent for the Precipitation of Sulfate," J. Chem. Soc., pp. 4216-4218 (1952).

412. Borkovskii, A. A., "Determination of Sulfate in Soluble Fluorides," Zavodskaya Lab., 3:1089-1090 (1934).

Fixation of F as BF_4 ion to remove interference.

413. Costagnou, R., "Solubility of Barium and Calcium Sulfates," Bull. Soc. Pharm. Bordeaux, 90:25-29 (1952).

Separation of Ba/Ca SO_4 mixture.

414. Chaterjee, K. P., "Determination of the Sulfate Ion by Precipitation as Barium Sulfate," Z. Anorg. Allgem. Chem., 121:128-134 (1922).

HCl > 0.1% as a source of error in precipitation with $BaCl_2$.

415. Dhandhukia, M. M., "Rapid Method of Sulfate Estimation," *Salt Res. Ind.*, **5**(1):17-18 (1968).

$BaSO_4$ precipitate-wash and weigh.

416. Environmental Protection Agency, "Methods for Chemical Analysis of Water and Wastes," EPA-625/6-74-003, p. 283 (1974).

Sulfate-gravimetric method uses APHA and ASTM methods.

417. Fales, H. A., "Factors Influencing the Determination of Sulfate as Barium Sulfate," *Ind. Eng. Chem., Anal. Ed.*, **11**:206-213 (1939).

Can remove KNO_3 interference by addition of HCl.

418. Fischer, R. B., "Rapid Precipitation of Barium Sulfate," *Anal. Chem.*, **25**:1544-1548 (1953).

In-depth study of precipitation of $BaSO_4$ with $BaCl_2$.

419. Friend, J. A. N., "Determination of the Sulfate Ion by Precipitation as Barium Sulfate," *Analyst*, **57**:559-562 (1932).

Early $BaCl_2$ procedure for $SO_4^=$ in Li_2SO_4; $SO_4^= \le 0.02$ N.

420. Gerarde, H. W., "Toxicological Studies on Hydrocarbons. VII. A Gravimetric Method for the Determination of Inorganic and Ethereal Sulfate in Urine," *Amer. Ind. Hyg. Assoc. J.*, **21**:511-514 (1960).

Rapid simplified method using quantitative self-regulating pressure filtration technique with barium.

421. Germuth, F. G., "The Occlusion of Barium Chloride by Barium Sulfate," *Am. J. Pharm.*, **99**:271-274 (1927).

Discussion of temperature factor in precipitation of $SO_4^=$.

422. Girman, "A Rapid Method for Determining Sulfates," *Novoe v Praktike Hidrogenizatii Zhirov, Sbornik Vsesoyuz. Nauch.-Issledovatel. Inst. Zhirov.*, pp. 127-129 (1939), *Khim. Referat. Zhur*, No. 3, p. 55 (1940).

$SO_4^=$ in Ni catalysts by volume of $BaSO_4$ precipitate in centrifuge tube.

423. Gottschalk, G., "Gravimetric Determination of Sulfate as Benzidine Sulfate," Z. anal. Chem., 155:251-263 (1957).

Sulfate detected by analysis of Ni wire, Fe plate, ZnO_2, H_2O, and methylene blue; metal ions removed by ion exchange and $PO_4^{\equiv}$ as $MgNH_4PO_4$; S to ± 0.05 mg.

424. Hahn, F. G., "Composition of Analytical Precipitates of Barium Sulfate," Z. Anorg. Allgem. Chem., 206:398-406 (1932).

Precipitate weight error due to formation of H_2SO_4.

425. Isakov, P. M., "Rapid Gravimetric Method of Determining Sulfate Ion," Nauch. Byull. Leningrad. Gosudarst. Univ., 13:8-10 (1946).

Adds picric acid to hasten $BaSO_4$ precipitation, improve size and form of crystal, and ease filtration.

426. Karoglanov, Z., "Causes of Contamination of Precipitates. I. Precipitation Reactions in which Barium Compounds Participate," Z. anal. Chem., 106:129-146 (1936).

Examines contamination of precipitate; believes errors due to contamination during early stages rather than adsorption phenomena.

427. Kolthoff, I. M., "The Determination of Sulfate as Barium Sulfate," Z. anal. Chem., 58:49-69 (1919).

428. Kolthoff, I. M., "The Gravimetric Determination of Sulfate as Barium Sulfate," Pharm. Weekblad., 56:122-142 (1919).

Literature review of $BaSO_4$ determinations with conclusions.

429. Kolthoff, I. M., "The Determination of Sulfates as Strontium Sulfate," Z. anal. Chem., 58:20-23 (1919).

430. Kolthoff, I. M., "The Determination of Sulfates as Strontium Sulfate," Pharm. Weekblad., 56:159-161 (1919).

Free acids and certain salts are disturbing factors and use of 50% EtOH makes solubility sufficiently low.

431. Kolthoff, I. M., "Determination of Sulfate According to F. Hahn at Extreme Dilution," Z. anal. Chem., 63:392-404 (1923).

432. Kolthoff, I. M., "Sulfate Determination According to Hahn at Great Dilutions," *Pharm. Weekblad.*, 60:1177-1190 (1923).

Hahn's method ($SO_4^=$ + Ba salt in boiling H_2O) combined with Winkler's method (filtering on asbestos); Precipitation in AcOH better than HCl; codeine-HCl, $PO_4^{\equiv}$, Ca all interferents.

433. Ledoux, L., "Application of Mechanical Precipitation to the Determination of Sulfuric Acid, Sulfates, Calcium, and Potassium," *Bull. Soc. Chim. Belg.*, **28**:51-52 (1914).

Mechanical agitation in cold with pure HCl and 2% $BaCl_2 \cdot 2H_2O$; filtered, washed with H_2O and ignited.

434. Mahr, C., "A New Method for Determining Sulfate," *Z. anal. Chem.*, **128**: 477-484 (1948).

$SO_4^=$ detected by precipitation of $[Co(NH_3)_6]BrSO_4$; precipitated $SO_4^=$ may be determined gravimetric or dissolved in water and Br detected by titration with $AgNO_3$ or Co detected colorimetrically.

435. Majdel, I., "Effect of Phosphoric Acid on the Determination of Sulfate with Barium Chloride," *Bull. Soc. Chim. Roy. Yougoslav.*, **1**(2):25-28 (1931).

$SO_4^=$ determined with $BaCl_2$ in presence of P_2O_5 and HCl; increase in P_2O_5 or $BaCl_2$ increases error while increase in HCl decreases error; recommends removal of P_2O_5 prior to analysis.

436. Majer, V., "Practical Importance of Winkler's Procedures for Determining Calcium, Lead, Sulfate and Phosphate," *Chem. Zentr.*, **1**:782 (1942).

437. Majer, V., "The Practical Significance of the Winkler Procedure," *Z. anal. Chem.*, **122**:257-262 (1941).

Winkler method useful in some cases but not as good or bad as some feel.

438. Margolina, S. S., "Analysis of Products of Chlorination of Oxides and Sulfides of Copper," *Zavodskaya Lab.*, **4**:861-863 (1935).

With $BaCl_2$ and Na_2SO_4.

439. Marjanovic, V., "Determination of Sulfate Ion as Barium Sulfate," Arhiv Hemiju, 1:5-18 (1927).

Cl$^-$, NO$_3^-$, Na, K, Mg, Fe, Cu, Al, and NH$_4$ do not interfere; PO$_4^=$ gives high value and Ca low value. Uses HCl and BaCl$_2$; solution < 0.3 g SO$_4^=$.

440. Matsui, M., "The Determination of the Sulfate Content of Sodium Sulfate," J. Chem. Ind., 24:1039-1053 (1921).

Examined five methods of BaSO$_4$ precipitation using pure Na$_2$SO$_4$.

441. Meillere, G., "Determination of H$_2$SO$_4$ and Sulfates," J. Pharm. Chem., 19:296-297 (1919).

Precipitation by BaCl$_2$ in slightly AcOH medium and near 100°.

442. Meldrum, W. B., "Determination of Sulfate in the Presence of Chromate," Ind. Eng. Cehm., Anal. Ed., 13:456-457 (1941).

Precipitate BaCl$_2$, weigh, fuse NaCO$_3$, detect CrO$_4$ in precipitate iodometrically.

443. Montequi, R., "Systematic Investigation of Anions," Anales Soc. Espan. Fis. Quim., 30:567-599 (1932).

SO$_4^=$ precipitate in AcOH solution by Ba(OAc)$_2$.

444. Oka, S., "Rapid Analysis by Centrifugal Methods," Japan Analyst, 1:136-140 (1952).

Quantitative analysis by volume measurement of BaSO$_4$ after centrifuging studied.

445. Orlov, I. E., "Rapid Method for Determining the Sulfate Ion by Means of a 'Coupled' Precipitation," Z. anal. Chem., 98:326-329 (1934).

BaSO$_4$ precipitated with BaCl$_2$ in presence of AlCl$_3$; Al precipitated by NH$_4$OH to methyl red;Al precipitate coagulates BaSO$_4$.

446. Owells, B. R., "Estimation of Barium Sulfate in the Presence of Silica," Chemist Analyst, 31:6 (1942).

BaSO$_4$ weight in Gooch crucible.

447. Owen, E. C., "Determination of Sulfates. A Study of the Conditions Necessary for the Precipitation of Benzidine Sulfate, with Special Reference to the Estimation of Sulfates in Urine," Biochem. J., 30: 352-360 (1936).

Use pH of 2.75, must remove phosphate before precipitate; chlorides do not interfere.

448. Pel'sh, G. K., "A Rapid Semimicromethod for the Determination of Ions by Weighing the Precipitates in Centrifuge Tubes," Uchenye Zapiski Leningrad. Gosudarst. Univ. im. A. A. Zhdanova; No. 211, Ser. Khim. Nauk, (15):105-115 (1957).

Simplified method of gravimetric determination; $BaSO_4$ precipitate centrifuged, dried, weighed.

449. Peskova, V. M., "Rapid Determination of the Sulfate Ion," Zavodskaya Lab., 9:1329-1330 (1940); Chem. Zentr., 2:571 (1942).

Adds saturated picric acid and excess 5% $BaCl_2$.

450. Pil'nik, R. S., "Rapid Gravimetric Method for Determination of Sulfate in Sodium Dichromate and Chromic Anhydride (in technical grade products)," Tr. Ural'sk. Nauchn.-Issled. Khim. Inst., (11):46-48 (1968).

$SO_4^=$ precipitation as $BaSO_4$ in presence of NaOAc to mask Cr^{+3}.

451. Pribil, R., "Use of Complexions in Chemical Analysis. XXXV. Gravimetric Determination of Barium and Sulfates," Chem. Listy, 45:542-544 (1951); Collection Czechoslav. Chem. Communs., 16:398-404 (1951).

Interfering Al, Cr, and Fe bound in acidic EDTA solutions during precipitation with barium nitrate.

452. Rabovskii, G. V., "Determination of Sulfate in Presence of Chromates," Zavodskaya Lab., 3:592-593 (1934).

$BaSO_4$ precipitation.

453. Radmacher, W., "Determination of Sulfur Dioxide and Sulfur Trioxide in Boiler Gases," Staub (Düsseldorf), 18:174-176 (1958).

Gravimetric determination of SO_2 and $BaSO_4$ expedient rather than nephelometric; need to provide absorbent with 0.1 N H_2SO_4 for quantitative precipitation.

454. Rudnev, N. A., "Effect of Nitric Acid on Precipitation of Barium Sulfate," Uchenuie Zapiski Kazan. Gosudarst. Univ., 90:1054-1061 (1930).

Increasing NO_2^- concentration gives increasing error to a definite limit, whereupon error decreases; washing with hot water frees Ba^+ ion.

455. Rudnev, N. A., "Precipitation of Barium Sulfate in the Presence of Chloride and Bromide Ions," Trans. B. Inst. Chem. Tech. Kazan, 1: 143-156 (1934).

Effect of HCl or HBr on precipitate is investigated.

456. Schleicher, A., "A New Possible Source of Error in the Determination of Sulfate as Barium Sulfate," Z. anal. Chem., 121:90-92 (1942); Neues Jahrb. Mineral., Geol. Ref. I, p. 15 (1942).

Adsorption of $BaCl_2$by filter paper; wash filter with cold HCl and hot H_2O prior to use.

457. Shereshevskii, I. L., "Methods of the Analysis of Sulfide-Hydrosulfide Liquors," Z. anal. Chem., 105:110-112 (1936).

Treats sample consecutively to determine $CO_3^=$, $HCO_3^=$, Cl^-, $SO_4^=$ (as $BaSO_4$), $SO_3^=$, $S^=$.

458. Shinkai, S., "A New Method of Chemical Analysis. I.," J. Soc. Chem. Ind., 40:348 (1937).

Improved method using $BaCl_2$.

459. Shinkai, "A New Method of Chemical Analysis. II. Determination of Anions," J. Soc. Chem. Ind., 40:349 (1937).

Comparative results of analyses.

460. Shinkai, S., "Rapid Determination of Sulfate in Common Salt," Japan Analyst, 3:330-331 (1954).

$BaSO_4$ precipitation.

461. Shlapin, V. M., "Precipitation of Barium Sulfate in the Presence of Ferric Salts," Uchenuie Zapiski Kazan. Gosudarst. Univ., 88:461-464 (1928).

Errors due to presence of Fe^{+++} may be partially compensated for by having a large excess of Fe^{+++}.

462. Specker, H., "Quantitative Separation of Inorganic Ions by Ion-Exchange on Alginic Acid," Z. anal. Chem., 141:33-38 (1954).

Separation of Fe, Cu, et al., for gravimetric determination of SO_4 using $BaCl_2$.

463. Spencer, G. C., "Report on Chemical Reagents (Determination of Sulfates in Ammonium Nitrate)," J. Assoc. Offic. Agr. Chem., 11:421 (1928).

$SO_4^=$ sample digested with concentrated HCl in Kjeldahl flask--Ba^{++} precipitate.

464. Toth, A., "Apparent Volume of the Solid Phase of Centrifuged Precipitates. III. Rapid Analysis of Sulfates by Measuring the Volume of Centrifuged Precipitates of Barium Sulfate," Acta Chim. Acad. Sci. Hung., 16:251-266 (1958).

465. Toth, A., "The Volume of Centrifuged Precipitates. III. A Rapid Method for the Estimation of Sulfate by Measuring the Volume of the Centrifuged Barium Sulfate Precipitate," Magyar Kem. Folyóirat, 61:239-245 (1955).

0.1 N HCl + 25% NH_4Cl + 1% $BaCl_2$ at 85° plus sample; after cooling and centrifuging, volume of precipitate read directly and $SO_4^=$ calculated.

466. Vasil'eva, L. A., "Precipitation of Barium Sulfate in Presence of Hydrochloric and Nitric Acids, in the Cold," Trans. Kirov Inst. Chem. Tech. Kazan, 4(5):97-105 (1935).

HNO_3 and HCl are interferences (coprecipitators).

467. Winkler, L. W., "Gravimetric Analysis. XII. Estimation of Sulfuric Acid," Z. Angew Chem., 33(1):59-60 (1920).

Add K_2CO_3, boil and add $BaCl_2$ solution; weigh precipitate x 1.0045.

468. Winkler, L. W., "Gravimetric Analysis. XIII. Determination of Sulfuric Acid," Z. Angew Chem., 33(1):159-160, 162-163 (1920).

1% NH_4Cl prevents interference with $BaCl_2$.

NEPHELOMETRIC AND TURBIDIMETRIC

469. Adams, D. F., "Tentative Method of Analysis of the Sulfation Rate of the Atmosphere," Health Lab. Sci., 8(4):243-247 (1971).

Added sulfaspend reagent and determined absorbance at 450 nm.

470. Alekseeva, M. V., "Methods for the Determination of Small Concentrations V. Determining Sulfate, Sulfite, and Sulfide," J. Applied Chem., 7:616-622 (1934).

$BaSO_4$ - Visual comparison with standards in flat bottom test tubes.

471. Aoyama, S., "Colorimetric Estimation of Turbidity of Silver Chloride and Barium Sulfate," J. Pharm. Soc. Japan, 48:702-712 (1928).

AgCl standard cannot be used for $BaSO_4$ precipitate.

472. APHA, "Turbidimetric Method (156 C)," in Standard Methods for the Examination of Water and Wastewater, 13th ed., pp. 334-335 (1971).

Details of $SO_4^=$ turbidimetric method using barium.

473. ASTM, "Standard Methods of Test for Sulfate Ion in Water and Wastewater (D 516); Method B-Turbidimetric Method," in Annual Book of ASTM Standards, 31:427-430 (1974).

Details of turbidimetric method using barium.

474. Baumann, A. N., "Automated Sampling and Analysis of Wet Process Phosphoric Acid Digestion Systems," in Automation in Analytical Chemistry, Technicon Symposia, 1967, Vol. I., pp. 257-260, Mediad, Inc., White Plains, N. Y. (1968).

Turbidimetric determination using $BaCl_2$ at 520 mμ; hot slurry sampling.

475. Blanc, P., "A Semimicromethod for the Determination of the Sulfate Ion," Trov. Soc. Pharm. Montpellier, 14:333-334 (1954).

5 to 50 mg/liter $BaSO_4$ in 20% "Tween 20."

476. Boutwell, P. W., "Determination of Sulfur in Urine," Ind. Eng. Chem., Anal. Ed., 4:117 (1932).

Early $BaCl_2$ - photometric.

477. Boyars, C., "Turbidimetric Method for Determination of Potassium Sulfate in Propellent Powders," *Anal. Chem.*, **20**:87 (1940).

$BaSO_4$ against standardized curve.

478. Claudy, H. N., "Automatic Sulfate Ion Analyzer," *Anal. Chem.*, **31**(7):1255-1258 (1959).

$BaSO_4$ colloidal solution; $SO_4^=$ concentration of 1 to 4%.

479. Coleman, R. L., "Turbidimetry Via Parallel Photometric Analysis Determination of Sulphate," *Anal. Chem.*, **44**(6):1031 (1971).

(GeMSAEC) technique using CAD and BaCl.

480. Denis, W. J., "Sulphates in Blood," *J. Biol. Chem.*, **49**:311-317 (1921).

$BaSO_4$ method for blood sulphate.

481. Environmental Protection Agency, "Methods for Chemical Analysis of Water and Wastes," EPA-625/6-74-003, pp. 277-278 (1974).

Sulfate-Turbidimetric method; uses APHA and ASTM methods.

482. Ferrara, L. W., "Turbidimetric Determination of Sulfate by the Auto-Analyzer: Sulfur in Plant Materials by Digestion with Nitric and Perchloric Acid," in *Automation in Analytical Chemistry*, Technicon Symposia, 1965, pp. 109-111, Mediad, Inc., White Plains, New York (1966).

Turbidimetric method at 420 mμ; 10-50 ppm; $BaSO_4$ in gelatin.

483. Gelman, C., "Estimation of Water-Soluble Chlorides, Sulfates, and Nitrates in Suspended Atmospheric Dusts," *J. Air Poll. Cont. Assoc.*, **7**:216-219 (1957).

Sample through Whatman 41H paper, weighed, extracted with C_6H_6, ion-exchanged and $SO_4^=$ determined by $BaSO_4$-turbidimetric method.

484. Haff, A. C., "An Automated Procedure for the Analysis of Total and Inorganic Sulfate in Serum and Urine," in *Advances in Automated Analysis*, Technicon International Congress, 1969, Vol. I., Clinical Research, Mediad, Inc., White Plains, N. Y. (1970).

Turbidimetric procedure using $BaCl_2$ precipitation and gelatin; 420 mμ.

485. Hibbard, P. L., "Turbidimetric Estimation of Precipitates," Ind. Eng. Chem., 16:804-807 (1924).

Construction and use of early optical instrument.

486. Hobin, N. K., "Turbidimetric Determination of Soluble Sulfates in Water-Soluble Color Additives," J. Ass. Offic. Anal. Chem., 53(2): 242-243 (1970).

$BaSO_4$ precipitation, turbidimetric measurement at 440 mμ; color additives adsorbed on activated charcoal.

487. Hofer, K., "A New Rapid Determination of Sulfate by the Method of Turbidity Measurements," Chem. Zentr., 2:3372 (1931); Wärme, 54:803-804 (1931).

Instrument for approximation of sulphate in boiler water and fuels (Ba^{++}).

488. Holy, H. W., "Automated Turbimetric Techniques," in Automated Analytical Chemistry, Technicon Symposium, 1963, pp. 113-116, Technicon Instruments Company, Ltd., Chertsey, England (1964).

$SO_4^=$ by turbimetric barium method; comparison with gravimetric and volumetric.

489. Huey, N. A., "Determination of Sulfate in Atmospheric Suspended Particulates; Turbidimetric Barium Sulfate Method," U.S. Pub. Health Serv. Publ., 999-AP-11, I-1-I-4 (1965).

Turbidimetric method limit is 50 γ $SO_4^=$; nephelometric method limit is 2 γ $SO_4^=$.

490. Huey, N. A., "The Lead Dioxide Estimation of Sulfur Dioxide Pollution," J. Air Poll. Contr. Assoc., 18(9):610-611 (1968).

Lead sulfate converted to lead carbonate; $SO_4^=$ determined by turbidimetric method at 450 mμ.

491. Jackson, D. D., "Turbidimetric Determination of Sulphate," J. Am. Chem. Soc., 23:799 (1901).

Range 1-60 mg using $Ba(OH)_2$.

492. Keily, H. J., "Nephelometric Determination of Sulfate Impurity in Certain Reagent Grade Salts," Anal. Chem., 27:759-764 (1955).

$SO_4^=$ precipitate with $BaCl_2$ crystals in EtOH - 0.2 to 10.0 ppm.

493. Koteneva, T. V., "The Use of a Colorimeter-Nephelometer in the Analysis of Very Soluble Salts," *Trudy Nauch.-Issledovatel. Inst. Geol. Arktiki, Ministerstva Geol. i Okhrary Nedr S.S.S.R.*, **98**(1):130-138 (1959).

$SO_4^{=}$ precipitate with $Ba(NO_3)_2$ compared with standard solution containing 20 mg. $SO_4^{=}$.

494. Lebedeva, M. I., "Turbidimetric Titration of Sulfate Ion in Mixed Solvents," *Tr. Tambov. Inst. Khim. Mashinostr.*, (7):128-131 (1971).

Phototurbidimetric titration of $SO_4^{=}$ in presence of Na_2CO_3, Na_2SO_3, Na_3BO_3, Na_3PO_4, and $Na_2Cr_2O_7$ based on precipitation of $SO_4^{=}$ as $CdSO_4$ in HOAc-EtOH, by titration with Cd^{++}, and measurement of absorbance.

495. Lindsay, F. K., "Method for Analysis of Boiler Scales and Sludges," *Ind. Eng. Chem., Anal. Ed.*, **12**:461 (1940).

Turbidimetric, $BaCl_2$, HCl.

496. Lopez-Rubio, F. B., "Rapid Determination of Sulfates by Nephelometry," *Ion*, **5**:689-693 (1945).

Obsolete $BaSO_4$ techniques.

497. Milton, R., "Determination of the Mineral Content of Foods by Wet Oxidation and Absorptiometric Methods," *Analyst*, **69**:299-302 (1944).

Sample oxidized in NH_4NO_3-HNO_3 solution; $SO_4^{=}$ by turbidity using Ba^{++}.

498. Narozhnykh, E. A., "Phototurbimetric Determination of Small Amounts of Sulfuric Acid in a Chromium Electrolyte," *Khim Khim. Tekhnol*, pp. 102-105 (1970), from Ref. *Zh. Khim*, (1971).

Reduction of Cr^4 to Cr^3 before $BaSO_4$ precipitate.

499. Nelson, G., "The Automatic Determination of Phosphate and Sulfate in Wet Process Phosphoric Acid," *Proc. ISMA, Tech. Conf.*, Edinburgh, 1965.

Iso-PrOH inhibits precipitation of $BaSO_4$; turbidimetric procedure using $BaCl_2$.

500. Omiti, S., "Hygienic Chemistry of Dust in Air. II. Turbidimetric Determination of Sulfate Ion in Water-Soluble Matter Collected by Deposit Gauge," Bunseki Kagaku, 12(11):1032-1037 (1963).

$BaSO_4$ turbidimetrically at 370 mμ; ± 5% in 10-150 ppm $SO_4^=$.

501. Osborn, R. A., "Turbidity and Color Measurements. I. A Photoelectric Cell Arrangement for Measuring Small Quantities of Certain Impurities in Reagent Chemicals," J. Assoc. Official Agr. Chem., 17:135-141 (1934).

Early photocell experiments.

502. Ozaki, T., "Phototransistor for the Turbidimetric Determination of Sulfate," Bunseki Kagaku, 8:672-673 (1959).

Replacement of photocell with phototransistor in photometer.

503. Parr, S. W., "Determination of Sulfur by Means of Turbidimeter," Ind. Eng. Chem., Anal. Ed., 3:66 (1931).

Turbidimetric of Sulfates using $BaCl_2$. Boiler water, circa 2,000 ppm. SO_4.

504. Pieters, H. A., "Nephelometric Determination of the Sulfate Ion," Chem. Weekblad, 29:188-189 (1932).

Construction details and preparation of standards (Ba^{++} method).

505. Pucherna, J., "The Determination of Sulfates with an Objective Photometer," Listy Cukrovan, 54:376 (1936).

Coal analysis 40-160 mg/liter. $BaCl_2$-Turbidimetric-6% error.

506. Rossum, J. R., "Suggested Method for the Turbidimetric Determination of Sulfate in Water," J. Am. Wat. Works Assoc., 53:873-876 (1961).

Discussion of procedure and interferants; $BaCl_2$ precipitation; color, turbidity, organic matter, and some inorganics interfere.

507. Rubia, P., "Turbidity of Barium Sulphate," Inform. Quim. Anal., 5:1-6 (1951).

Beer's law validation.

508. Rudy, R. B., "Sulphuric/anhydride in Portland Cement," J. Research Natl. Bur. Standards, 16:555 (1936).

Early photometric development-$BaSO_4$.

509. Sheen, R. T., "Turbidimetric Determination of Sulfate in Water," Ind. Eng. Chem., Anal. Ed., 7(4):262-265 (1935).

Turbidimetric - Application of Tyndall Effect; $BaSO_4$

510. Singer, E., "Turbidimetric Estimation of Sulfates," Chem. Prumsyl, 11:526-527 (1961).

Precipitate with EtOH and glycerol using $BaCl_2$.

511. Steinbergs, A., "Determination of Sulphur," J. Australian Inst. Agr. Sci., 17:155 (1951).

Sample digested; turbidimetric determination of $BaSO_4$ against standards.

512. Steinbergs, A., "Determination of Total Sulfur in Soils," Analyst., 80:457-461 (1955).

Ultimate determination as $SO_4^=$ by turbidity using Ba^{++}.

513. Steinbergs, A., "Rapid Turbidimetric Method for the Determination of Small Amounts of Sulfur in Plant Material," Analyst, 78:47-53 (1953).

Sample digested; turbidimetric determination of $BaSO_4$ against standards.

514. Takiyama, K., "Electron Microscopic Study on the Suspension in the Nephelometry of Sulfate Ion," Japan Analyst, 3:291-293 (1954).

Particle-size control with EtOH and gelatin using $BaCl_2$.

515. Technicon, "Sulfate in Water and Wastewater," Technicon Industrial Method No. 39-69W, Tarrytown, N. Y. (1969).

Turbidimetric at 520 mμ; silica and color interfere using $BaCl_2$.

516. Thomas, J. F., "A Turbidimetric Sulfate Determination," Wat. and Sew. Works, 101:462-465 (1954).

$SO_4^=$ solution; NaCl, $BaCl_2$; determined at 380 mμ; $SO_4^=$ concentration determined from calibration curve.

517. Toennies, G., "Photonephelometric Microdetermination of Sulfate," Anal. Chem., 25(1):160-165 (1953).

$BaSO_4$ in H_2O-EtOH-glycol system. 01-100 ppm.

518. Treon, J., "Rapid Turbidimetric Method for Determination of Sulfates," Ind. Eng. Chem., Anal. Ed., 14:119 (1942).

Turbidimetric method using Duboscq colorimeter and Ba^{++}.

519. Umemoto, H., "Simple Semiquantitative Determination of Sulfate Ion," Japan Analyst, 2:34 (1953).

Graduated black bar with brass disc for immersion in $BaSO_4$ slurry.

520. Verduyn, G., "Automatic Determination of Sulfates by an Improved Nephelometric Method," Atmos. Environ., 8:707-715 (1974).

Automatic nephelometric determination of $SO_4^=$ using Barium perchlorate ppm; as low as .1 ppm/ml $SO_4^=$.

521. Vladimirov, L. V., "Simplified Nephelometric Method of Determining Sulfate in Acid Extracts," Zavodskaya Lab., 3:707-710 (1934).

Procedure described for $BaSO_4$.

522. Voth, J. L., "Coprecipitation of Sodium in Sulfate Determination. A Spectrographic Method," Anal. Chem., 31(6):1094-1095 (1959).

Examination of Na co-precipitate in $SO_4^=$ precipitate with $BaCl_2$.

523. Wickbold, R., "Photometric Precipitation Titration for Determining Traces of Sulfate," Angew Chem., 65:159-161 (1953).

.03-1.5 mg. $SO_4^=$ General discussion of factors affecting precipitation titration. $BaSO_4$ as example.

524. Wimberley, J. W., "The Turbidimetric Determination of Sulfate Without the Use of Additives," Anal. Chim. Acta., 42(2):327-329 (1968).

$SO_4^=$ in rock samples turbidimetrically using $BaCl_2$ at 380 mμ; Beer's law obeyed for 10-100 ppm $SO_4^=$ (1 cm cell) and 5-25 ppm $SO_4^=$ (4 cm cell).

525. Zdybek, G., "Determination of Microgram Quantities of Sulfate in Organic Linkages," Anal. Chem., 32(4):559 (1960).

$BaSO_4$ in EtOH-Dipropylene Glycol-Chloric acid system.

RADIOMETRIC

526. Armento, W. J., "Determination of Sulfate with Chromium-51," *Anal. Chem.*, **35**(7):918-920 (1963).

    $SO_4^=$ precipitated with $BaCr^{51}O_4$ in HCl. Neutralization with NH_4 precipitates excess $BaCr^{51}O_7$ and remaining excess $Cr^{51}O_4$ is gamma counted.

527. Bruna, A., "Development of a Radiometric Method for the Automatic Determination of Phosphates and Sulfates in Aqueous Solution," *Communicate Eur. Energ. At.-EURATOM (Rapp.)*, EUR-3738F (1968).

    Sulfates to $Sr^{89}SO_4$ in the presence of dioxane which reduced the solubility of $SrSO_4$ in H_2O.

528. Ehrenberg, R., "Radiometric Microanalysis," *Mikrochem. Pregl. Festschr.*, pp. 61-63 (1929).

    Uses ThB as radioactive material. Radiotagged titration.

529. Ehrenberg, R., "Radiometric Micro-Analysis. II, " *Biochem. Z.*, **172**: 10-16 (1926).

    Radiotagged titration Pb isotope.

530. Forrest, J., "Sampling and Analysis of Atmospheric Sulfur Compounds for Isotope Ratio Studies," *Atmos. Environ.*, **7**(5):561 (1973).

    Sulfur concentrations measured by Ag^{110} tracer.

531. Owens, C. W., "Rapid Ion-Exchange Separation of Radioactive Sulfur Anions," *Radiochem. Radioanal. Lett.*, **13**(5-6):325-327 (1973).

    S_{35}-contg. anions ($SO_4^=$ incl.) separated on Rexyn 201; monitored by passing effluent through quartz tubing packed with plastic scintillator beads mounted on photomultiplier tube.

532. Tolgyessy, G., "Radiometric Titration with Tagged Potassium Ferrocyanide Measuring Solution," *Magyar Kem. Folyoirat*, **65**:149-152 (1959).

    Discussion of classical method and automatic activity-measuring device.

533. Yatsimirskii, K. B., "Radiometric Titration with Solutions of Complex Compounds of Cobalt-60," *Trudy Komissii Anal. Khim., Akad. Nauk S.S.S.R. Inst. Geokhim. i Anal. Khim.*, **9**:194-199 (1958).

    $SO_4^=$ precipitated with $[Co^{60}(NH_3)_6]Cl_3$

SPECTROPHOTOMETRIC

534. Agterdenbos, J., "Theoretical Considerations on the Indirect Determination of Anions. Determination of Sulfate with Barium Chloranilate," Talanta, 11:875-885 (1964).

Ba Chloranilate at 332 mμ.

535. Andersen, L. "Spectrophotometric Method for Determining Sulfate and Organic Sulfur on the Micro- and Ultramicro Scale," Acta. Chem. Scand., 7:689-692 (1953).

Spectrophotometric Modification of Benzidine Method.

536. Barney, J. E., II, "Determination of Sulphate with Barium Cholranilate," Talanta, 12:425 (1965).

Discussion

537. Basargin, N.N., "Photometric Determination of Traces of Sulfate Ions and Sulfur by Using Nitchromazo," Zh. Anal. Khim., 23(5) 732-735 (1968).

$SO_4^=$ determined using a Barium-nitchromazo complex and a green filter (640 mμ); absorbance compared with standards.

538. Bertolacini, R. J., "Colorimetric Determination of Sulfate with Barium Chloranilate," Anal. Chem., 29(2):281-283 (1957).

Absorption at 530 mμ. 50% EtOH solution.

539. Bertolacini, R. J., "Ultraviolet Spectrophotometric Determination of Sulfate, Chloride, and Floride with Chloranilic Acid," Anal. Chem., 30:202-205 (Correction 498) (1958).

Absorption at 332 mμ. Useful up to 150 ppm.

540. Bostrom, E. E., "Improvement in Automatic Colorimetric Determination tion of Low Concentrations of Sulfate," Atmos. Envirn., 1(5); 599 (1967).

Use of flourosilicone tubing for pumping diozane on technicon.

541. Carlson, R. M., "Modification to Increase Sensitivity of Barium Chloranilate Method for Sulfate," Anal. Chem., 39(6):688-690 (1967).

Absorbance in visible region 50% EtOH. Buffer of H_3PO_4 and KH_2PO_4 intensifies the color.

542. Egami, F., "Sulfate Microdetermination," *Bull. Chem. Soc. Japan*, **30**: 442-457 (1957).

$SO_4^=$ precipitated as $BaSO_4$; excess Ba^{++} precipitated as $BaCrO_4$; excess $CrO_4^=$ estimated in alkaline solution at 375 mμ; 30 to 900 γ SO_4.

543. EPA, "Methods for Chemical Analysis of Water and Wastes," EPA-625/6-003, pp. 279-282 (1974).

Sulfate-Automated Chloranilate Method.

544. Eriksen, T. E., "Direct Spectrophotometric Determination of Sulfate in Aqueous Solutions of Sulfur Dioxide," *Acta Chem. Scand*., **26**(8): 3337-3341 (1972).

$SO_4^=$ determination by $FeSO_4^+$ method; SO_2 and HSO_3^- masked with H_2CO. Modification of Goguel Method.

545. Gales, M. E., "Determination of Sulfate by Automatic Colorimetric Analysis," *Analyst*, **93**(1103):97-100 (1968).

Technicon method using Ba Chloranilate determination at 520 mμ designed for 5 to 400 mg $SO_4^=/\ell$ in water.

546. Goguel, R., "Direct Spectrophotometric Detection of Sulfate in Natural Water by Formation of the Ferric Sulfate Complex," *Anal. Chem*., **41**(8): 1034-1038 (1969).

10 to 500 mg $SO_4^=/\ell$ using absorption of $FeSO_4^+$ complex at 325 and 360 nm.

547. Haslam, J. "The Detection of 'Additional Elements' in Plastic Materials by the Oxygen Flask Method," *Analyst*, **86**:239-248 (1961).

Sample burnt in oxygen; combustion products absorbed in NaOH; $SO_4^=$ detected colorimetrically by barium chloranilate or 4-amino-4'-chlorodiphenyl hydrochloride method.

548. Hinze, W. L., "Spectrophotometric Determination of Sulfate Ion with Barium Iodate and the Linear Starch Iodine System," *Anal. Chem*., **45**(4):814-815 (1973).

$SO_4^=$ detected spectrophotometrically by precipitation in EtOH with $Ba(IO_3)_2$; reduction of IO_3^- with I^- in starch and measurement of absorbance of starch - I complex at 625 or 587 nm; low ppm range.

549. Iwasaki, I., "Spectrophotometric Determination of a Small Amount of Sulfate Ion. I. Solid and Aqueous Barium Chromate Method," Nippon Kagaku Zasshi, 79:32-38 (1958).

Acid suspension of $BaCrO_4$ used to precipitate $SO_4^=$. Excess Ba precipitated with NH_4OH. Exchanged excess CrO_4 determined with diphenyl carbohydrazine by absorption at 545 mμ; 0.2 to 12 γ $SO_4^=$ to 20 to 100 ppm.

550. Iwasaki, I., "Spectrophotometric Determination of a Small Amount of Sulfate Ion. II. Barium Chromate Suspension Method," Nippon Kagaku Zasshi, 79:38-44 (1958).

Sample, $BaCrO_4$ suspension, ammonia, $CaCO_3$, alcohol; centrifuge; compare filtrate at 370 mμ with standard; 0.3 to 100 ppm to 100 to 500 mg $SO_4^=$.

551. Iwasaki, I., "Spectrophotometric Determination of a Small Amount of Sulfate Ion. III. Determination of Traces of Sulfate, 0.2-5 ppm," Nippon Kagaku Zasshi, 79:44-50 (1958).

$BaCrO_4$, sample, acetate buffer, alcohol; centrifuge; filtrate; diphenyl-carbazide reagent, HCl; determine absorbancy at 545 mμ with 5 mm cells; PO_4 and Fe interfere.

552. Iwasaki, I., "Spectrophotometric Method for the Determination of Small Amounts of Sulfate Ions," Bull. Chem. Soc. Japan, 30:847-851 (1957).

0.3 to 100 ppm $SO_4^=$; $SO_4^=$ as $BaSO_4$ using $BaCrO_4$; if $<$ 20 ppm $SO_4^=$ - 545 mμ, if $>$ 20 ppm $SO_4^=$ - 370 mμ.

553. Kanno, S., "Improvements in the Barium Chloranilate Method [for Sulfate Determination]," Eisei Kagaku, 13(4):217-218 (1967).

Method improved with pH 5.2 instead of pH 4.0 buffer.

554. Kato, T., "Chemical Analysis by Ultraviolet Filter-Photometer. I. Determination of a Small Quantity of Sulfate Ion," J. Chem. Soc. Japan, Pure Chem. Sect., 76:373-376 (1955).

BaCrO Method. CrO_4 absorption measured at 366 or 405 mμ; 2 to 120 per ml.

555. Klein, B., "Microdetection of Sulfate," Ind. Eng. Chem., Anal. Ed., 16:536 (1944).

Benzidine sulphate, diazotized, and coupled with N(1-naphthyl) ethylenediamine·2HCl. Intense purple color.

556. Klipp, R. W., "Determination of Sulfur Traces in Napthas by Lamp Combustion and Spectrophotometry," Anal. Chem., 31(4):596-597 (1959).

Sample burned in ASTM lamp; resulting H_2SO_4 detected by barium chloranilate method at 330 or 530 mμ; 1 to 400 ppm.

557. Klockow, D., "Amplification Method for Determination of Particle-Sulfate in Background Air," Atmos. Environ., 7(2):163-168 (1973).

$SO_4^=$ converted with $Ba(IO_3)_2$. 6 x amount of iodine is obtained. Absorbed at 504 or 366 nm. Working range 0.4 to 4.0 μg. Sulfur.

558. Lambert, J. L., "Colorimetric Determination of Sulfate Ions," Anal. Chem., 27:800-801 (1955).

$SO_4^=$ determined by amount of dye released from an insoluble thorium borate-Amaranth lake; measured at 521 mμ; up to 400 ppm $SO_4^=$; HCO_3 and Fe interfere.

559. Lambert, J. L., "Colorimetric Determination of Sulfate Ion," Anal. Chem., 27:1835 (1955).

Thorium borate-Amaranth dye. Direct proportional dye release with $SO_4^=$. 0 to 400 ppm.

560. Lambert, J. L , "Determination of Fluoride Ion Using a Monohydroxy Azo Dye-Thorium Lake," Anal. Chem., 26(3):558-560 (1954).

Use of dye. (Related to $SO_4^=$ ion work.)

561. Lambert, J. L., "Simplified Preparation of Cadmium Iodide-Linear Starch Reagent for Colorimetric Iodometry," *Anal. Chem.*, **35**(3): 405 (1963).

Preparation of reagent.

562. Laxton, J. W., "Automatic Monitor for Recording Sulfur Trioxide in Flue Gas," *J. Inst. Fuel*, **37**(276):12-17 (1964).

Ba chloranilate at 535 mμ; 0.2 to 100 ppm SO_3; automatic system.

563. Lazrus, A. L., "A New Colorimetric Microdetermination of Sulfate Ion," in *Automation in Analytical Chemistry*, Technicon Symposia, 1965, pp. 291-293, Mediad, Inc., White Plains, New York (1966).

Colorimetric-methylthymol blue method at 480 mμ; 0.5 to 50 ppm $SO_4^=$.

564. Lazrus, A. L., "New Automated Microanalyses for Total Inorganic Fixed Nitrogen and for Sulfate Ion in Water," *Advan. Chem. Ser.*, (73): 164-171 (1968).

$BaSO_4$-methylthymol blue; 0.5 to 50 ppm $SO_4^=$.

565. Lloyd, A. G., "The Use of Barium Chloranetate in the Determination of Enzymically Liberated Sulphates," *Biochem.*, **72**:133 (1959).

566. Marenzi, A. D., "A Micromethod for the Determination of Sulfates and Its Application to Plasma, Serum, and Urine," *Anales Farm Bioquim.*, **8**:62-74 (1937).

$SO_4^=$ determined colorimetrically as difference between sample phosphotungstomolybdic acid solution and unprecipitated benzidine.

567. Marenzi, A. D., "Application of the Palfrich Photometer to the Determination of Sulfates by the Method of Marenzi and Banti," *Anales Farm Bioquim.*, **10**:77-81 (1939).

Blood sulfates. Benzidine-phosphotungstomolybdic acid.

568. Matsuo, T., "Application of Benzidine and Its Derivatives in Analytical Chemistry," *J. Japan Chem.*, **8**:588-592 (1954).

Review of use of benzidine as precipitating reagent for colorimetric determination of $SO_4^=$.

569. Mendes-Bezerra, A. E., "Determination of Sulfate by Titrimetric and Colorimetric Measurement of Equivalent Displaced Zinc Ion," *Anal. Lett.*, **1**(6):355-358 (1968).

200 μg to 100 mg $SO_4^=$; two methods titration of excess EDTA with Zn and spectrophotometric determination of Ba-EDTA complex with excess Zn (treated with Zincon).

570. Morgan, G. B., "Automated Laboratory Procedures for the Analyses of Air Pollutants," Anal. Instrum., 4:101-112 (1966).

Sampling on glass-fiber filter; preparation; $SO_4^=$ determination by automated methylthymol blue method.

571. Nasu, T., "Spectrophotometric and Fluorimetric Determination of Micro Amounts of Sulfate Using Thorium-Flavonol Complex," Bunseki Kagaku, 19(5):673-680 (1970).

Measure decrease in absorbance at 390 nm or fluorescence at 470 nm of fluorescence complex. F^- and PO_4^{3-} interfere.

572. Pacheco, J. de la R., "Photometric Applications of the Chromate-Meta-bisulfite Reaction," Infom. Quim. Anal., 4:119-126 (1950).

Chromate-meta-bisulfite reaction can be applied to determination of Ba, PG, Hg, and $SO_4^=$.

573. Persson, G. A., "Automatic Colorimetric Determination of Low Concentrations of Sulfate for Measuring Sulphur Dioxide in Ambient Air," Air and Water Pollut. Int. J., 10:845-852 (1966).

$SO_4^=$ precipitated with $Ba(ClO_4)_2$; excess Ba indicated with Thorin. Technicon procedure 0 to 10 γ/ml. 0.3 γ threshold.

574. Prevost, S., "Spectrophotometric Study of Pyrocatechol Violet-Thorium Complexes in Aqueous Solution of pH 3.2 and the Reaction of Sulfate Ions with These Complexes," J. Chim. Phys., 64(10):1533-1539 (1967).

Method for determination of $SO_4^=$ in 0 to 100 γ/ml range.

575. Schafer, H. N. S., "An Improved Spectrophotometric Determination of Sulfate with Barium Chloranilate as Applied to Coal Ash and Related Materials," Anal. Chem., 39(14):1719 (1967).

80% IPA as solvent. Absorbance of chloranilate 310 nm.

576. Stanford Research Institute, "Size Determination of Atmospheric Sulfate and Chloride Particles," HEW Contract No. PH-86-64-54.

Ba chloranilate method evaluated.

577. Stoffyn, P., "Spectrophotometric Micro and Submicro Determination of Sulfur in Organic Substances with Barium Chloranilate," Anal. Chem., 36(2):397-400 (1964).

Sample mineralized by oxidation; $SO_4^{=}$ determined by Ba chloranilate; interferences removed by ion exchange with ammonium Dowex 50; 0.3 to 100 µg S.

578. Technicon, "Sulfate in Water and Wastewater," Technicon Industrial Method No. 118-71W/Tentative, Tarrytown, New York (1972).

$BaSO_4$-methylthymol blue.

579. Werner, O., "Colorimetric Determination of Nonmetals," Z. Ver. Chem., Beih, 48:113-120 (1944); Chem. Zentr., 2:1305 (1944).

Critical review on determination of F, Cl, Cl^-, H_2S, $SO_4^{=}$, P, $PO_4^{=}$, etc.

580. Wharton, W. H., "Application of Spectrophotometric Titrations to Micromolar Solution of Calcium, Magnesium, Oxilate, or Sulfate," Anal. Chem., 36(8):1679-1681 (1964).

Titration with $Ba(ClO_4)_2$; 80% EtOH, Thorin indicator. See endpoint at 550 mµ.

SUBSTITUTED BENZIDINES

581. Belcher, R., "Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. Part I. Solubilities of the Sulfates," J. Chem. Soc., pp. 544-546 (1951).

Development of new reagents for $SO_4^=$ determination.

582. Belcher, R., "Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. Part II. Reaction with Oxidizing Agents," J. Chem. Soc., pp. 546-547 (1951).

Reactions of new reagents with oxidizers.

583. Belcher, R., "Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. Part XII. Reagents for the Precipitation of Sulphate," J. Chem. Soc., pp. 1334-1337 (1953).

Sulfates of 4-amino-4'-halogenodiphenyls prepared; discussion.

584. Belcher, R., "Some Factors Influencing the Solubilities of Amine Sulfates," Anal. Chim. Acta., 8:122-129 (1953).

Discussion and development of 4:4'-diaminotolane.

585. Belcher, R., "4,4'-Diaminotolan as a Reagent for the Titrimetric Determination of Sulfate," Anal. Chim. Acta., 8:146-149 (1953).

Replaces benzidine; phosphate and cromate interfere.

586. Belcher, R., "The Titrimetric Determination of Sulphate with 4-Amino-4'-Chlorodiphenyl Hydrochloride as Reagent," Analyst, 81:4-8 (1956).

25 to 100 mg $SO_4^=$ in 100 ml or 2.5 to 25 mg $SO_4^=$ in 50 ml; PO_4 interferes.

587. Coleman, R. L., "Turbidimetry via Parallel Photometric Analysis," Anal. Chem., 44:1031-1034 (1972).

$SO_4^=$ determined by parallel photometry using $BaCl_2$ and 4-amino-4'-chlorodiphenyl hydrochloride.

588. Dodgson, K. S., "The Determination of Inorganic Sulphate in the Study of Sulphatases," Biochem. J., 55:436 (1953).

Add benzidine and filter. Unreacted benzidine measured colorimetrically after thymol addition.

589. Dodgson, K. S., "A Preliminary Account of the Glycosulphtase of Littorina Littorea," Biochem. J., 57:310 (1954).

Add benzidine and filter. Add thymol and measure colorimetrically.

590. Dodgson, K. S., "A Preliminary Account of the Chondrosulphatase of Proteis Vulgaris," Biochem. J., 65:131 (1957).

Add benzidine and filter. Unreacted benzidine and thymol and measure colorimetrically.

591. Haslam, J., "The Detection of 'Additional Elements' in Plastic Materials by the Oxygen Flask Combustion Method," Analyst, 86:239-244 (1961).

S reduced to $SO_4^=$; $SO_4^=$ detected with barium chloride (700 mμ), barium chloranilate (530 mμ) or 4-amino-4'-chlorodiphenyl hydrochloride (700 mμ) methods.

592. Hovorka, V., Chem. Listy, 36:113 (1942).

Monoacetylated and monobenzoylated benzidines give precipitates with sulfates. N,N'-diacetylbenzidine give only a faint precipitate. Vanillyledenebenzidine used as a sulfate reagent reported. Other mono- and di-methines derived from benzidine were reported as giving precipitates with sulfate.

593. Jones, A. S., "A Spectrophotometric Method for the Determination of Sub-micro Quantities of Sulphur with 4-Amino-4'-chlorodiphenyl," Analyst, 81:15-18 (1956).

30 to 120 μg $SO_4^=$; determined by UV spectrophotometry of reagent difference between blank and sample after precipitation.

594. Jones, A. S., "A Submicro Method for the Estimation of Sulfur," Chem. and Ind., 662(23):662-663 (1954).

Precipitate with 4-amino-4'-chlorodiphenyl hydrochloride in presence of surface-active agent; determined by UV at 254 mμ.

595. Jones, P. A., "The Indirect Spectrophotometric Determination of the Sulphate Ion with 2-Aminoperimidine," *Anal. Chim. Acta.*, 64:85-92 (1973).

Precipitation of $SO_4^=$ with 2-aminoperimidine hydrochloride; measure excess reagent at 305 nm; 4-120 ppm $SO_4^=$.

596. Maddalone, R. F., "Determination of Sulfate by Thermal Reduction of Perimidylammonium Sulfate," *Anal. Chem.*, **47**(2):316-319 (1975).

$SO_4^=$ precipitation as perimidylammonium sulfate; thermal decomposition of precipitate and excess reagent yields SO_2; determined by West-Gaeke or flame photometric procedures.

597. Martin, J. M., "An Improved Colloidal Stabilizer for Use in the Nephelometric Determination of the Sulfate Ion," *Anal. Chim. Acta.*, **39**:252-258 (1967).

$SO_4^=$ determined using 4-amino-4'-chlorodiphenyl hydrochloride and acid gum ghatti; determined to 1 ppm $SO_4^=$.

598. Martin, J. M., "The Nephelometric Determination of Small Amounts of Sulphate Ion," *Anal. Chim. Acta.*, **39**:175-180 (1967).

$SO_4^=$ determined nephelometrically using 4-amino-4'-chlorodiphenyl hydrochloride, peptone, and gum ghatti; 2.5-25 ppm $SO_4^=$ in 10 ml aliquots.

599. McClure, G. L., "An Improved Synthesis of 2-Perimidylammonium Ion for Use as a Sulfate Reagent," *Anal. Chim. Acta.*, **64**:289-291 (1973).

Description of synthesis procedure.

600. Nietzki, R., *Ber.*, **18**:3255 (1805).

Solubility of naphlhedine sulphate reported to be less than benzidine sulphate.

601. Raistrick, H., "A Survey of Fungal Metabolism of Inorganic Sulphates," *Biochem. J.*, **43**:90 (1948).

Add benzidine, dissolve precipitate in NaOH and titrate ppt with standard $BaCl_2$ and Na rhodizonate.

602. Slack, H. G. B., "The Metabolism of Sulphated Polysaccharides," Biochem. J., 65:459 (1957).

Unreacted, add benzidine and filter benzidine and thymol and measure colorimetric.

603. Stephen, W. I., "A New Reagent for the Detection and Determination of Small Amounts of the Sulfate Ion," Anal. Chim. Acta., 50:413-422 (1970).

Discussion of 2-aminoperimidine synthesis and use; determination of 0.2 ppm $SO_4^=$.

604. Van Loon, J. P., Chem. Zent., Volume II, 1669 (1908).

Solubility of substituted benzidines and related compounds given. O-tolidine sulfate solubility was 1.2 g/liter at room temperature.

605. Welcher, F. J., "Specific and Selective Organic Reagents," Proc., Int. Symp. on Microchemistry, Birmingham University, England, 20-27 August 1958, pp. 6-21 (1960).

Theory. Discussion of properties, synthesis and use of organic reagents. Makes example of Belchers work.

606. Wilkinson, H. C., "The Use of 4-Amino-4'-chlorodiphenyl Hydrochloride for the Determination of Sulphur in Coal," Analyst, 81:9-11 (1956).

Bomb combustion of coal; add 4-amino-4'-chlorodiphenyl hydrochloride solution, filter; titrate precipitate with NaOH using phenol red-bromothymol blue indicator.

MISCELLANEOUS-METHODS

607. Albee, A. L., "Correction Factors for Electron Probe Microanalysis of Silicates, Oxides, Carbonates, Phosphates, and Sulfates," Anal. Chem., 42(12):1408-1414 (1970).

Discussion of correction parameters.

608. Altshuller, A. P., "Atmospheric Sulfur Dioxide and Sulfate: Distribution of Concentration at Urban and Nonurban Sites in the United States," Environ. Sci. and Tech., 7(8):709-712 (1973).

Comparisons of $SO_4^=$ concentration over country.

609. Antisari, O. V., "Research in Chemical Composition of Some Forms of Atmospheric Particles," Chicago Univ., Dept. Meteorol., Tech. Note 5 (1956).

Identification of particle size and chemical composition by Liesegang Rings in treated gel.

610. Anyz, F., "A Contribution to the Detection of the Aerosols Containing Sulphate Particles," Tellus, 18:216-220 (1966).

Sulphate aerosol detection by Liesegang Rings in treated gelatin ($BaCl_2$).

611. Bavika, L. I., "Determination of Sulfuric Acid in Air by a Vanadate Method," Neftepererab. Neftekhim., 9:40-41 (1971).

Air sample passed through ammonium vanadate solution; yellow color formed with H_2SO_4.

612. Becka, J., "Quantitative Analysis by Means of the Refractometer and Interferometer," Z. Physiol. Chem., 121:288-299 (1922).

Calculating percentage of substance precipitated from solution by difference in refraction.

613. Braun, T., "Applications of Precipitation Membranes in Analytical Chemistry," Talanta, 11(11):1543-1544 (1964).

Precipitation membranes eliminate need for separation of precipitate in colorimetric, radiometric titrations, and radioactive precipitate exchanges.

614. Cadle, R., "Micrurgic Identification of Chloride and Sulfate," National Acad. Sci.--National Res. Council Pub. No. 652, pp. 18-21 (1959).

Microscopic identification of particulates.

615. Crider, W. L., "Hydrogen Flame Chemiluminescence Detector for Sulfate in Aqueous Soltuions," Anal. Chem. Acta., 47(2):237-241 (1969).

$SO_4^=$ determination to 2 μg $SO_4^=$/ml solution; specific $SO_4^=$ analyzer in H_2O_2 determination of SO_2.

616. Deniges, G., "Rapid Identification of the Two Ions in Barium Sulfate," Bull. Soc. Chim., 27:560-564 (1920).

Microscopic qualitative for Ba and $SO_4^=$; violet color from SO_4 + $Na_2(CN)_5NO$.

617. Deniges, G., "Silver Nitrate as a Microchemical Reagent for the Sulfate Ion," Bull. Soc. Pharm. Bordeaux, 64:57-60 (1926).

Dry sample and add 3% $AgNO_3$. Crystals are characteristic in photomicrograph.

618. Dube, G., "Semi-Automated Thermometric Titration of Sulfate," Anal. Chem., 47(2):285-289 (1975).

$BaSO_4$ precipitation using $BaCl_2$; thermometric titration.

619. Duval, C., "Thermogravimetry of Analytical Precipitates. XLIII. Determination of Sulfur," Anal. Chim. Acta., 4:623-628 (1950).

Pyrolysis curves traced; discussion.

620. Environmental Protection Agency, "Air Quality Data for 1968 from the National Air Surveillance Networks and Contributing State and Local Networks," EPA Pub. No. APTD-0978 (1972).

Sampling; determination by automated methylthymol blue method at 480 nanometers.

621. Forbes, E. A., "Determination of Microgram Amounts of Sulfate by Emission Spectroscopy of Barium with a Nitrous Oxide-Acetylene Flame," Analyst, 98(1168):506-511 (1973).

$SO_4^=$ determined indirectly in aqueous solutions by Ba emission at 553.55 nm; $K_2C_2O_4$ $(NH_4)_2C_2O_4$, Na_3VO_4, $NiCl_2$, NaF, and $HClO_4$ interfered if in $SO_4^=$ solution.

622. Francis, W. E., "The Measurement of the Dewpoint and Sulfuric Acid Vapor Content of Combustion Products," GRB 64, The Gas Research Board, The Abbey, Southend Road, Beckenham, Kent.

Dewpoint measured by electrical conductivity; H_2SO_4 estimate unsuccessful due to trapping difficulty.

623. Frey, H., "Determination of Sulfate," *Anal. Chem. Acta.*, **6**:126-132 (1952).

Various methods described (volumetric, turbidimetric, microvolumetric, colorimetric, ignition, photometric); ion exchange to remove metal interference.

624. Freze, N. A., "Determination of Sulfate Ion by Filtration Titration," *Zavod. Lab.*, **8**(10-11):1181-1182 (1939); *Khim. Referat. Zhur.*, **5**:68 (1940).

Addition of $BaCl_2$ to $SO_4^=$ solution with repeated filtration until no precipitation formed.

625. Freze, N. A., "Determination of Sulfates by Hydrostatic Suspension," *Zavod. Lab.*, **14**:997-998 (1948).

$BaSO_4$ suspension subjected to a d. determination; $BaSO_4$ filtered off and d. of filtrate measured.

626. Fukae, M., "Determination of Sulfates," *Rinsho Byori, Rinjizokan*, (17):116-123 (1970).

Review of determination of biologic and inorganic sulfate.

627. Green, W. D., "Identification of Chemical Constituents in Single Aerosol Particles," *Amer. Chem. Soc., Div. Water Air Waste Chem., Preprints*, **7**(2):83-90 (1967).

$SO_4^=$ identified by precipitation of $BaSO_4$ in glycerol-gelatin films containing a soluble Ba salt.

628. Gurevich, V. G., "Chronometric Microanalytical Method," *Nekotorye Voprosy Farmatsii, Sbornik Nauch. Trudov, Vyssh. Farm. Ucheb. Zavedenii Ukr. S. S. R.*, pp. 89-93 (1956).

Measuring the time taken to form a precipitate with $BaCl_2$.

629. HEW, "Air Pollution Measurements of the National Air Surveillance Network. Vol. I. Analyses of Suspended Particulate, 1953-1957," Pub. Health Ser. Pub. No. 637 (1958).

Determination by turbidimetric method using $BaCl_2$ at 500 mμ; also determination in a glycerin-alcohol solution.

630. HEW, "Air Quality Criteria for Sulfur Oxides," NAPCA Pub. No. AP-50 (1969).

Sampling; determination by colorimetry (MTB) and turbidity.

631. Hogstrom, U., "Residence Time of Sulfurous Air Pollution from a Local Source During Precipitation," *Ambio*, **2**(1-2):37-41 (1973).

Weather conditions affect residence time.

632. Huygen, C., "The Determination of Sulfate by the Ring Oven Technique and Its Application to Air Pollution Measurement," *Mikrochim. Ichnoanal. Acta*, pp. 6-9 (1963).

Qualitative detection to 0.1 μg.

633. Ivlev, L. S., "Optical Constants for Atmospheric Aerosols," *Izv. Vyssh. Vcheb. Zaved. Fiz.*, **15**(5):91-97 (1972).

Optical constants for compounds present in atmosphere (including $SO_4^=$) determined using spectrometry.

634. Jahr, K. F., "Dilatometrically Indicated Titrations. I. Precipitation of Sulfate Ions as Barium Sulfate," *Fresenius Z. Anal. Chem.*, **241**(2): 110-121 (1968).

$BaSO_4$ using dilatometer to indicate volume changes; Na and NH_4 interfere.

635. Karekar, N. V., "Adsorption of Sulfate Ion by Thorium Hydroxide Solutions, Dialyzed to Different Degrees," *Kolloid-Z.*, **68**:286-289 (1934).

Coagulation of $Th(OH)_4$ hydrosol determined for K, Mg, and Al sulfates in presence of MeOH, EtOH, and iso-proOH.

636. Kellogg, W. W., "Sulfur Cycle," Science, 175 (4022):587-596 (1972).

Broad discussion.

637. Kenny, F., "Volumetric Determination of Sulfate by Titration of Excess Lead Nitrate with Potassium Chromate with Siloxene Indicator," Anal. Chem., 29(4):543-546 (1957).

$SO_4^=$ precipitate as $PbSO_4$; excess Pb titration in dark chamber with $K_2Cr_2O_4$; end-point determined by photometric determination of siloxene-emitted light.

638. Kullbom, S. D., "Combined Infrared and X-Ray Spectrometric Method for Determining Sulfonate and Sulfate Concentrations of Detergent Range Alkylbenzene Sulfonate Solutions," Anal. Chem., 37(8):1031-1034 (1965).

Special application for determination of Na_2SO_4 in detergent slurry.

639. Lawson, J. R., "Infrared Determination of Trace Amounts of Polyatomic Inorganic Ions," Anal. Chem., 40(3):636-639 (1968).

Solid solutions in alkali, halide crystals; fusion in KBr disks for spectrophoto at 9 and 16 μ.

640. LeGuyon, R. F., "Micro - Titration of Sulfate Anions and Barium Cations with the Aid of the Micro - Centrifuge," Bull. Soc. Chim., 41:1387-1389 (1927).

Discussion of $BaSO_4$ precipitation using centrifuge.

641. LeGuyon, R. F., "Volumetric Micro-Analysis and Centrifugo-Volumetry," Ann. Chim., 10:50-112 (1928).

Discussion of various centrifuge-volumetric methods.

642. Leroux, J., "Average Composition of Particulate Air Pollutants as Disclosed by X-Ray Techniques," Int. J. Environ. Anal. Chem., 1(2):131-140 (1971).

General discussion and collection of data.

643. Lodge, J. P., "An Improved Method for the Detection and Estimation of Micron Sized Sulfate Particles," Anal. Chim. Acta, 29(4):372-374 (1963).

Identification limit 2 x 10^{-15} g $SO_4^=$ using filters treated with $BaCl_2$ and K_2 rhodizonate.

644. Lyshkow, N. A., "Apparatus and Method for Analysis of Gas Streams," U.S. Patent 3,712,793 (Cl. 23-232E; G oln), 23 January 1973.

Chemiluminescent reaction of sample and thin-layer reagent; SO_2 by ozone reagent.

645. Miyahe, Y., "The Chemical Nature of the Saline Matter in the Atmosphere," Geophys. Mag. Japan, 16(1):64-65 (1948).

General discussion.

646. Monkman, J. L., "Gas Champer Microapparatus in Identification of Air-Borne Pollutants," Anal. Chem., 27(5):704-708 (1955).

Slides coated with glycerol- and benzidine-treated water sulfate show under polarized light all sulfates react.

647. Nebbia, L., "Determination of Sulfur Trioxide in Mixtures Containing Sulfur Dioxide and Air," Chim. Ind., 52(2):158-160 (1970).

Samples determined by potentiometric titration and gas chromatography for SO_3; 1-10% SO_3 content.

648. Ngo, H. D., "Separation of Some Cations and Anions by the Ring Oven Technique," Mikrochim. Acta, 6:935-938 (1972).

Description of multiple ion (Fe, Ni, Mn, Al, Cd, Cu, Co, SO_4, Cl, NO_3) separation method.

649. Novakov, T., "Chemical Composition of Pasadena Aerosol by Particle Size and Time of Day. III. Chemical States of Nitrogen and Sulfur by Photoelectron Spectroscopy," J. Colloid. Interface Sci., 39(1):225-234 (1972).

Determination of chemical state of S in smog particles as function of particle size and time of day; $SO_4^{=}$ in larger particles, predominating during day; SO_2 in smaller particles, predominating at night.

650. Pearson, F. J., "Chemical Composition of Atmospheric Precipitation in Northeastern United States," U.S. Geol. Surv., Water Supply Paper No. 1535-P (1971).

Discussion of monthly bulk precipitation rates at 18 northeastern sites.

651. Perchec, H., "Thermal Determination of Sulfate," Bull. Soc. Chim. France, 3:619-620 (1964).

Precipitation of $SO_4^=$ with $Ba(NO_3)_2$ done in covered Dewar; exothermic temperature plotted versus total volume; break at end-point.

652. Pieters, H. A. J., "Determination of Sulfate," Chem. Weekblad, 39:20-23 (1942).

Review of nongravimetric methods (benzidine method of Raschig, tetrahydroxyquinone indicator, colorimetric with $BaCrO_4$, nephelometric, conductometric, measurement of $BaSO_4$ precipitate in graduated centrifuge tube).

653. Ponomareva, L. K., "Photochronometric Determination of Sulfates," Zavod. Lab., 32(1):16-17 (1966).

Add to sample HCl and heat to boil, add H_3BO_3 and filter. Add $BaCl_2$ and measure time to absorbance change of 0.1.

654. Popoff, S., "Microscopic Examination of Precipitation as an Aid to Precise Analysis. I. Estimation of Sulfates as Barium Sulfate," Ind. Eng. Chem., Anal. Ed., 2:45-54 (1930).

Effects of titration technique on crystal formation.

655. Pribil, R., "Contributions to the Basic Problems of Complexometry. I. The Blocking of Indicators and Its Elimination," Talanta, 3:91-94 (1959).

Discussion.

656. Rissmann, E. F., "Infrared Method for Rapid Analysis of the Sulfate Content in Reacted Lime and Limestone Materials," Anal. Chem., 42(13): 1628-1632 (1970).

$SO_4^=$ in saturated EDTA/H_2O solution in 0.003 mm liquid cell for specphoto at 1,110 cm^{-1}.

657. Samuelson, O., "The Use of Base-Exchanging Substances in Analytical Chemistry. III.," Svensk. Kem. Tid., 52:115-125 (1940).

Review of $SO_4^=$ interferences and effect of using H^+ charged organolite.

658. Sander, A., "A New Simple Procedure for the Identification of the Most Important Sulfur-Oxygen Compounds," Chem. Ztg., 43:173 (1919).

HgCl$_2$ as reagent for spot test.

659. Shaw, R. W., "Sulfate Deposition by Precipitation into Lake Ontario," Water, Air, Soil Pollut., 2(1):125-128 (1973).

General discussion.

660. Stork, G., "Indirect Determination of Light Elements by X-Ray Fluorescence Analysis. II. Determination of Sulfate, Chloride and Bromide in Presence of Each Other, and Beryllium," Fresenius Z. Anal. Chem., 262(3):161-166 (1972).

Precipitate with BaCl$_2$; measured Kα lines; 48 µg.

661. Swinarski, A., "Rapid Methods for the Volumetric Determination of Sulfates and Phosphates with the Centrifuge," Przemysl Chem., 9:119-122 (1953).

Precipitation with BaCl$_2$, 0.4 M HCl; removal of Fe^{+++} and Al^{+++} not necessary.

662. Szal, J., "Determination of Sulfates," Wiad. Chem., 26(10):685-705 (1972).

A review.

663. Tai, H., "Infrared Spectrophotometry of Sulfate," Anal. Chem., 29(10): 143 (1957).

Freeze dry with KBr disk for IR spectrophotometry.

664. Tockstein, A., "Complexonate - Exchange Reactions as a Basis of Analytical Micromethods," Sbornik ved. praci, Vysoka skola Chem. Technol. Pardubice, pp. 139-154 (1959).

Discussion of EDTA-metal complex formation.

665. Tufts, B. J., "Chemical Identification of Halide and Sulfate in Submicron Particles," Anal. Chem., 30:3001 (1958).

Electron microscope; 25 ml H$_2$O, SAT with BaNO$_3$ PbNO$_3$.

666. Urone, P., "Chemistry of Sulfur Compounds in the Atmosphere," Air Water Poll., Proc. Summer Workshop, 1970, pp. 587-598 (1972).

A review.

667. Underwood, A. L., "Infrared Spectrophotometry of Aqueous Nitrate, Nitrite, and Sulfate Solutions," Anal. Chim. Acta., 29:79-81 (1963).

$SO_4^=$ band is cation dependent. CO_3, NH_4, and most organic compounds interfere.

668. Van Den Heuvel, A. P., "The Formation of Ammonium Sulfate in Water Droplets Exposed to Gaseous Sulfur Dioxide and Ammonia," Quart. J. Roy. Meteor. Soc., 89:271-275 (1963).

Mass of $SO_4^=$ proportional to product of drop surface area and exposure time.

669. Van Slyke, D. D., "A Gasometric Micromethod for the Determination of Iodates and Sulfates, and Its Application to the Estimation of Total Base in Blood Serum," J. Biol. Chem., 74:659-675 (1927).

$SO_4^=$ determined by gasometric estimation of iodate dissolved when $SO_4^=$ solution equilibrated with excess solid $Ba(IO_3)_2$.

670. Weisz, H., "A Color Reaction for Sulfates," Mikrochim Acta, 1:26-28 (1959).

Add one drop of 0.1% $Ba(NO_3)_2$ on filter paper plus Na rhodizonate, then one drop $AgNO_3$. Sulfate changes red to blue.

671. West, P. W., "Analytical Methods for the Study of Air Pollution," J. Chem. Educ., 46(2):96-98 (1969).

A review; emphasis on ring oven methods.

672. Williams, M. B., "Thermometric Titration of Sulfate," Talanta, 17(6): 548-551 (1970).

Titration with $Ba(ClO_4)_2$.

MISCELLANEOUS - BOOKS

673. Allport, N. L., Colorimetric Analysis, 2nd Ed., Vol. I, pp. 326-327, Chapman and Hall, Ltd., London (1957).

$SO_4^=$ in blood by benzidine precipitation.

674. Ayres, G. H., Quantitative Chemical Analysis, 2nd Ed., pp. 146, 219-223, 420, 582-585, Harper and Row, New York (1968).

Various methods (gravimetric: $BaSO_4$; titrimetric: reduction to H_2S which is determined iodometrically).

675. Bark, L. S., Thermometric Titrimetry, 1st Ed., pp. 57-58, Pergamon Press, Oxford, England (1969).

$BaSO_4$ precipitation and thermometric titration.

676. Belcher, R., New Methods in Analytical Chemistry, pp. 71-75, 84-86, 88-89, Reinhold Publishing Corporation, New York (1955).

Various methods and reagents (gravimetric: hexa-aminocobalt-III bromide, octa-amino-µ-amino-µ-nitrodicobalt-III nitrate; titrimetric: 4-chloro-4'-aminodiphenyl, 4:4'-diaminotolane).

677. Belcher, R., New Methods of Analytical Chemistry, 2nd Ed., pp. 72, 206-207, 284-285, 338-341, Reinhold Publishing Corporation, New York (1964).

Various methods, reagents, and indicators (titrimetric: rhodizonic acid, EDTA-Solochrome Black, Alizarin Red S; spectrophotometric: 4-amino-4'-chlorodiphenyl).

678. Berka, A., Newer Redox Titrants, 1st Ed., pp. 176-177, Pergamon Press, Oxford, England (1965).

Titration with hydroquinone.

679. Blaedel, W. J., Elementary Quantitative Analysis: Theory and Practice, pp. 213, 220-225, 343-344, 517, 650-651, Row, Peterson and Company, Evanston, Illinois (1957).

Various methods (gravimetric, turbidimetric, volumetric: benzidine).

680. Blaedel, W. J., *Elementary Quantitative Analysis: Theory and Practice*, 2nd Ed., pp. 213, 221-225, 290, 737-741, 884, Harper and Row, New York (1963).

Various methods (gravimetric; volumetric: thorin or dithizone; turbidimetric).

681. Blaedel, W. J., "High-Frequency Method of Chemical Analysis," in *Physical Methods in Chemical Analysis*, W. G. Berl, Ed., Vol. III, p. 130, Academic Press, Inc., New York (1956).

Titration of $SO_4^=$ with $Ba(NO_3)_2$.

682. Blasius, E., "Analytical Chemistry of Sulfur Compounds," in *Inorganic Sulphur Chemistry*, G. Nickless, Ed., pp. 201-205, Elsevier Publishing Company, Amsterdam (1968).

Various (gravimetric: Ba, Sr, benzidine; volumetric: Ba, Pb, etc.; polarographic; photometric; nephelometric; flame-photometric; radiometric).

683. Burkhalter, T. S., "High Frequency Conductometric (Impedimetric) Titrations," in *Comprehensive Analytical Chemistry*, C. L. Wilson, Ed., pp. 245-246, Elsevier Publishing Company, Amsterdam (1964).

With barium acetate.

684. Brezina, M., *Polarography in Medicine, Biochemistry, and Pharmacy*, pp. 118-120, Interscience Publishers, Inc., New York (1958).

$SO_4^=$ determined indirectly by effect on lead or barium ion wave.

685. Britton, H. T. S., *Conductometric Analysis*, p. 109, Chapman and Hall, Ltd., London (1934).

Titration with $Pb(NO_3)_2$.

686. Britton, H. T. S., "Conductometric Analysis," in *Physical Methods in Chemical Analysis*, W. G. Berl, Ed., Vol. II, p. 96, Academic Press, Inc., New York (1951).

$SO_4^=$ in drinking water; titration with lithium oxalate.

687. Brumblay, R. U., A First Course in Quantitative Analysis, pp. 297-304, 362-366, Addison-Wesley, Reading, Massachusetts (1970).

Gravimetric as $BaSO_4$; volumetric with Calmagite or Erio-T as indicator and EDTA as titrant.

688. Charlot, G., Colorimetric Determination of Elements, pp. 74, 389-390, Elsevier Publishing Company, Amsterdam (1964).

Discussion and listing of methods but no procedures (adsorption chromatography; rhodizonate photometry; turbidimetric; colorimetric: barium chloranilate; reduction to S(II)).

689. Christian, G. D., Atomic Absorption Spectroscopy, pp. 440-441, Wiley-Interscience, New York (1970).

Indirect AA using excess cation determination.

690. Conley, R. T., Infrared Spectroscopy, 2nd Ed., pp. 202-203, 207, Allyn and Bacon, Inc., Boston (1972).

$SO_4^=$ bands at 1,130 to 1,080 cm^{-1} and 680 to 610 cm^{-1}.

691. Crow, D. R., Polarography, p. 106, Methuen and Company, Ltd., London (1968).

Amperometric titration with $Pb(NO_3)$.

692. Cumming, A. C., in Quantitative Chemical Analysis, R. A. Chalmers, Ed., 11th Ed., pp. 104-105, 202-203, 260-262, Oliver and Boyd, Edinburgh, Scotland (1956).

Volumetric (after reduction to H_2S, H_2S determined with methyl red as indicator; as $BaSO_4$ using sodium rhodizonate as indicator); gravimetrically as $BaSO_4$.

693. Davis, D. G., "Conductometric Titrations," in Comprehensive Analytical Chemistry, C. L. Wilson, Ed., Vol. IIA, p. 205, Elsevier Publishing Company, Amsterdam (1964).

Conductometric (barium acetate).

694. Davis, D. G., "Potentiometric Titrations," in Comprehensive Analytical Chemistry, C. L. Wilson, Ed., Vol. IIA, pp. 132-135, Elsevier Publishing Company, Amsterdam (1964).

Potentiometric (Pb, Ba, membrane electrodes).

695. Dean, J. A., Flame Photometry, p. 267, McGraw-Hill Book Company, Inc., New York (1960).

Indirect determination of $SO_4^=$ by excess barium.

696. Dick, J. G., Analytical Chemistry, p. 347, McGraw-Hill Book Company, Inc., New York (1973).

General discussion of EDTA titration of excess barium.

697. Donbrow, M., Instrumental Methods in Analytical Chemistry. Vol. I. Electrochemical Methods, p. 256, Sir Isaac Pitman and Sons, Ltd., London (1966).

Conductometric titration of metal sulphate with $BaCl_2$ or acetate.

698. Donbrow, M., Instrumental Methods in Analytical Chemistry. Vol. II. Optical Methods, pp. 234-237, Sir Isaac Pitman and Sons, Ltd., London (1967).

Nephelometric determination.

699. Erdey, L., "Chemiluminescent Indicators," in Indicators, E. Bishop, Ed., Pergamon Press, Oxford, England (1969).

Chromatometric determination of $SO_4^=$ in presence of siloxene indicator.

700. Ewing, G. W., Instrumental Methods of Chemical Analysis, 3rd Ed., pp. 581-582, McGraw-Hill Book Company, Inc., New York (1969).

General textbook, turbidimetric experiment for $SO_4^=$.

701. Feigl, F., Chemistry of Specific, Selective and Sensitive Reactions, pp. 312-314, Academic Press, Inc., New York (1949).

Benzidine precipitation.

702. Flaschka, H. A., "Titrations with EDTA and Related Compounds," in *Comprehensive Analytical Chemistry*, C. L. Wilson, Ed., Vol. IB, pp. 365-366, Elsevier Publishing Company, Amsterdam (1960).

Titration of excess barium with EDTA.

703. Fowles, G., *Volumetric Analysis*, pp. 108-110, 153, 201, G. Bell and Sons, Ltd., London (1957).

Volumetric using barium oxalate, barium chromate, and benzidine.

704. Fritz, J. S., *Quantitative Analytical Chemistry*, 2nd Ed., pp. 54, 208-209, 513-515, 537-539, Allyn and Bacon, Inc., Boston (1969).

Gravimetric, volumetric (Alizarin Red S as indicator).

705. Furman, N. H., Ed., *Standard Methods of Chemical Analysis. Vol. I. The Elements*, 6th Ed., pp. 1007-1015, 2483-2484, D. Van Nostrand Company, Inc., Princeton, New Jersey, (1962).

Various $SO_4^=$ methods ($BaSO_4$: gravimetric; $BaCl_2$: K_2CrO_4 titrations; $BaCrO_4$: KI titration; benzidine hydrochloride titration; combustion; $BaSO_4$: turbidimetric).

706. Gilbert, P. T., "Nonmetals," in *Analytical Flame Spectroscopy*, R. Mavrodineanu, Ed., pp. 295-296, MacMillan and Company, Ltd., London (1970).

Indirect flame-emission determination of excess barium, AA spectroscopy.

707. Grant, J., Ed., *Clowes and Coleman's Quantitative Chemical Analysis*, 15th Ed., pp. 65-67, 172-174, J. A. Churchill, Ltd., London (1947).

Various methods (gravimetric: $BaSO_4$; volumetric: iodometric, benzidine).

708. Guilbault, G. G., *Practical Fluorescence*, pp. 228, 257, Marcel Dekker, Inc., New York (1973).

Quench by $SO_4^=$ of fluorescence of Th-morin complex.

709. Haddock, L. A. "Sulfur," in Comprehensive Analytical Chemistry, C. L. Wilson, Ed., Vol. IC, pp. 282-290, Elsevier Publishing Company, Amsterdam (1962).

General discussion of methods.

710. Haff, L. V., "Oxygen-Containing Inorganic Sulfur Compounds," in The Analytical Chemistry of Sulfur and Its Compounds, J. H. Karchmer, Ed., Part I, pp. 203-207, 210-212, 236, Wiley-Interscience, New York (1970).

Various methods (gravimetric; turbidimetric; spectrophotometric; by reduction to H_2S); separation by ion-exchange.

711. Headridge, J. B., Photometric Titrations, pp. 92, 99-100, 104, Pergamon Press, New York (1961).

Turbidimetric with $BaCl_2$ precipitation; automatic spectrophotometric titration at 520 mµ with barium perchlorate using thoron as indicator.

712. Hendrickson, E. P., "Air Sampling and Quantity Measurement," in Air Pollution, A. C. Stearn, Ed., 2nd Ed., Vol. II, pp. 3-52, Academic Press, Inc., New York (1968).

General sampling procedures.

713. Herrmann, R., "The Applications of Flame Photometry in Biology and Medicine," in Analytical Flame Spectroscopy, R. Mavrodineanu, Ed., p. 502, MacMillan and Company, Ltd., London (1970).

Indirect determination using excess barium in 873 nm band (BaOH).

714. Hillebrand, W. F., Applied Inorganic Analysis, 2nd Ed., pp. 711-723, John Wiley and Sons, New York (1953).

Discussion of methods (including errors) (gravimetric; volumetric; turbidimetric; colorimetric).

715. Hochgesang, F. P., "Nephelometry and Turbidimetry," in Treatise on Analytical Chemistry. Part I. Theory and Practice, I. M. Kolthoff, Ed., Vol. 5, pp. 3313-3314, 3317-3320, John Wiley and Sons (Interscience Publishers), New York (1964).

Automatic turbidimetric of $BaSO_4$.

716. Holy, H. W., "Automated Analytical Techniques in Water and Air Pollution," in Automated Analytical Chemistry, Technicon Symposium, 1963, pp. 9-14, Technicon Instruments Company, Ltd., Chertsey, England (1964).

General automated procedures including $SO_4^=$.

717. Huber, W., Titrations in Nonaqueous Solvents, pp. 136, 188-189, Academic Press, New York (1967).

Acidimetric using barium acetate which is back titrated potentiometrically; conductometric.

718. Ingram, G., "Micro-Analysis of Organic Compounds," in Methods of Quantitative Micro-Analysis, R. F. Milton, Ed., 2nd Ed., pp. 91-94, Edward Arnold (Publishers), Ltd., London (1955).

Gravimetric; volumetric.

719. Jacobs, M. B., The Chemical Analysis of Air Pollutants, pp. 41, 90, 116-117, Interscience Publishers, Inc., New York (1960).

Turbidimetric; sampling.

720. Katz, M., "Analysis of Inorganic Gaseous Pollutants," in Air Pollution, A. C. Stearn, Ed., 2nd Ed., Vol. II, pp. 54-80, Academic Press, Inc., New York (1968).

General analysis for sulfur compounds (West-Gaeke; H_2O_2: titration; conductimetric; iodometric; $BaSO_4$: turbidimetric; H_2S: methylene blue).

721. Klockow, D., "On the Determination of Sulphate in Background Air," in Abstracts, IUPAC International Congress on Analytical Chemistry, 3-7 April 1972, Kyoto, pp. 581-582 (1972).

Various methods (volumetric; nephelometric; iodometric; radiometric) and sampling.

722. Kolthoff, I. M., Polarography, 2nd Ed., Vol. II, pp. 558, 917-919, Interscience Publishers, New York (1952).

Indirect polarographic measuring effect on diffusion current of barium ion; amperometric titration using $Pb(NO_3)$.

723. Kolthoff, I. M., *Quantitative Chemical Analysis*, 4th Ed., MacMillan Company, London (1969).

General textbook.

724. Kolthoff, I. M., *Volumetric Analysis. Vol. I. Theoretical Fundamentals*, 2nd Ed., p. 98, Interscience Publishers, New York (1942).

Titration using $BaCl_2$ or lead; discussion.

725. Kolthoff, I. M., *Volumetric Analysis. Vol. II. Titration Methods*, 2nd Ed., pp. 163-165, 190-191, 203, 306-316, Interscience Publishers, Inc., New York (1947).

Determination with benzidine; $BaCl_2$ (hydrolytic precipitation); palmitate; $Pb(NO_3)_2$; sodium rhodizonate; tetrahydroxyquinone; fluorescein; methyl red.

726. Kolthoff, I. M., *Volumetric Analysis. Vol. III. Titration Methods*, pp. 292-293, 338-340, Interscience Publishers, Inc., New York (1957).

Reduction to H_2S with iodometric determination of sulfide; titration of chromate.

727. Kucharsky, J., *Titrations in Non-Aqueous Solvents*, pp. 73, 130-131, 136, 141, Elsevier Publishing Company, Amsterdam (1965).

Various methods (conductometric; potentiometric).

728. Landis, P. S., "Tetra- and Hexavalent Organosulphur Compounds," in *The Analytical Chemistry of Sulfur and Its Compounds*, J. H. Karchmer, Ed., Part II, pp. 792-793, 809, Wiley-Interscience, New York (1972).

Various methods (paper chromatography; IR spectroscopy; hydrolysis).

729. Lyalikov, Y., *Physicochemical Analysis*, pp. 366-368, Mir Publishers, Moscow (1968).

Conductomertic titration.

730. MacDonald, A. M. G., "Determination of Halogens and Sulphur in Organic Compounds," in *Comprehensive Analytical Chemistry*, C. L. Wilson, Ed., Vol. IB, pp. 533-539, Elsevier Publishing Company, Amsterdam (1960).

Gravimetric; volumetric; reduction of S; conductometric; amperometric; turbidimetric.

731. Milner, G. W. C., The Principles and Applications of Polarography and Other Electroanalytical Processes, pp. 317-318, 646-648, Longmans, Green and Company, London (1957).

Indirect polarographic by reduction to H_2S; amperometric titration.

732. Milton, R. F., "Colorimetric Analysis," in Methods of Quantitative Micro-Analysis, R. F. Milton, Ed., 2nd Ed., pp. 330, 406, 413-414, Edward Arnold (Publishers), Ltd., London (1955).

Colorimetric (diazotisation of benzidine); nephelometric.

733. Milton, R. F., "Illustrative Examples of Micro-Volumetric Procedures," in Methods of Quantitative Micro-Analysis, R. F. Milton, Ed., 2nd Ed., pp. 172-173, 195, 227-228, Edward Arnold (Publishers), Ltd., London (1955).

Volumetric using benzidine, tetrahydroxyquinone; $BaCr_2O_4$: diphenylcarbazide; EDTA.

734. Mitchell, A. D., Modern Methods in Quantitative Chemical Analysis, pp. 38-39, 136-137, Longmans, Green and Company, London (1932).

Volumetric (determination of excess Ba).

735. Passwater, R. A., Guide to Fluorescence Literature, Vol. I, II, Plenum Press, New York (1967, 1970).

Bibliography.

736. Patterson, G. D., Jr., "Sulfur," in Colorimetric Determination of Nonmetals, D. F. Boltz, Ed., pp. 267-270, 278, Interscience Publishers, Inc., New York (1958).

Turbidimetric; colorimetric determination using benzidine.

737. Price, W. J., Analytical Atomic Absorption Spectroscopy, p. 178, Heydon and Son, Ltd., London (1972).

Determination of excess barium.

738. Pungor, E., "Adsorption Indicators," in Indicators, E. Bishop, Ed., 1st Ed., p. 465, Pergamon Press, Oxford, England (1972).

Determination of $SO_4^{=}$ by titration using sodium alizarine sulphonate as surface precipitation indicator.

739. Pungor, E., Oscillometry and Conductometry, pp. 181-183, Pergamon Press, Oxford, England (1965).

Precipitation as $BaSO_4$; oscillometric determination.

740. Reilly, C. N., "High-Frequency Methods," in New Instrumental Methods in Electrochemistry, R. Delahay, Ed., p. 342, Interscience Publishers, Inc., New York (1954).

General discussion.

741. Savvin, S. B., Organic Reagents for Determining Barium and Sulfate Ions, Nauka, Moscow (1970).

Review.

742. Schwarzenbach, G., Complexometric Titrations, 2nd Ed., pp. 123, 315-318, Methuen and Company, Ltd., London (1969).

Volumetric (EDTA).

743. Skoog, D. A., Fundamentals of Analytical Chemistry, pp. 203-205, 631, Holt, Rinehart and Winston, New York (1963).

Gravimetric; amperometric titration.

744. Snell, F. D., Colorimetric Methods of Analysis, 3rd Ed., Vol. II, pp. 767-775, D. Van Nostrand Company, Inc., New York (1949).

Turbidimetric ($BaSO_4$); nephelometric ($BaSO_4$); colorimetrically (chromate: diphenylcarbazide, benzidine).

745. Snell, F. D., Colorimetric Methods of Analysis, 3rd Ed., Vol. IIA, pp. 671-674, D. Van Nostrand Company, Inc., New York (1959).

Reduction to H_2S (methylene blue); turbidimetric; nephelometric; colorimetric (thorium: amaranth lake, benzidine in UV, 4-amino-4'-chlorodiphenyl).

746. Snell, F. D., Commercial Methods of Analysis, 2nd Ed., pp. 111, 157-160, 166-168, 230-231, Chemical Publishing Company, Inc., New York (1964).

Various methods (barium rhodizonate; gravimetric; volumetric).

747. Steyermark, A., Quantitative Organic Microanalysis, 2nd Ed., pp. 110, 126, Academic Press, New York (1961).

Volumetric ($BaSO_4$: tetrahydroxyquinone).

748. Stock, J. T., Amperometric Titrations, p. 555, John Wiley and Sons (Interscience Publishers), New York (1965).

Indirect titration using bromate-arsenic (III) biamperometric titration.

749. Stock, J. T., "Electro-Chemical Methods of Micro-Analysis," in Methods of Quantitative Micro-Analysis, R. F. Milton, Ed., 2nd Ed., pp. 495-497, Edward Arnold (Publishers), Ltd., London (1955).

Amperometric titration.

750. Sutton, F., A Systematic Handbook of Volumetric Analysis or The Quantitative Determination of Chemical Substances by Measure, Applied to Liquids, Solids, and Gases, J. Grant, Ed., pp. 261, 438-442, 575, Butterworths Scientific Publications, London (1955).

Conductometric; chromate titration; potentiometric; amperometric; benzidine; $BaCl_2$ precipitation; gravimetric.

751. Tamamushi, R., "Application of Polarography and Related Electrochemical Methods to the Study of Labile Complexes in Solution," in Progress in Polarography, P. Zuman, Ed., Vol. III, pp. 35-36, 40-41, Wiley-Inter-Science, New York (1972).

Stability constants of $SO_4^=$ complexes.

752. Tölg, G., "Elemental Analysis with Minute Samples," in Wilson and Wilson's Comprehensive Analytical Chemistry, G. Svehla, Ed., Vol. III, pp. 101, 103, Elsevier Scientific Publishing Company, Amsterdam (1975).

Spectrophotometric; fluorimetric.

753. Tyrrell, H. J. V., Thermometric Titrimetry, pp. 95-96, 131, Chapman and and Hall, Ltd., London (1968).

$BaCl_2$ titration.

754. Vogel, A. I., A Text-Book of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis, 3rd Ed., pp. 276, 446-448, 462-468, 573, 806-807, 850-851, 958-959, 996-997, 1040-1041, Chaucer Press, Great Britain (1966).

Various $SO_4^=$ methods ($BaSO_4$: EDTA titration; $PbSO_4$: EDTA titration; Ba chloranilate: colorimetric; $BaSO_4$: nephelometric; potentiometric titration; high-frequency titration; amperometric titration).

755. Wagner, W., Advanced Analytical Chemistry, pp. 8, 206-207, Reinhold Publishing Corporation, New York (1956).

Volumetrically (benzidine, chromate, rhodizonic acid, tetrahydroxyquinone); gravimetric (benzidine, $BaSO_4$, hexamminocobalt (III) bromidesulfate); nephelometric.

756. Walden Research Corporation, Improved Methods for Sampling and Analysis of Gaseous Pollutants from the Combustion of Fossil Fuels. Vol. I. Sulfur Oxides, EPA Contract No. CPA-22-69-95 (1971).

General sampling and analysis procedures.

757. Walton, H. F., Principles and Methods of Chemical Analysis, pp. 106, 352, 391, 400, Prentice-Hall, Inc., New York (1952).

Volumetric (sodium rhodizonate, tetrahydroxyquinone); conductometric; amperometric.

758. Walton, H. F., Principles and Methods of Chemical Analysis, 2nd Ed., pp. 151, 177, Prentice-Hall, Inc., Englewood Cliffs, New Jersey (1964).

Ion-exchange (gravimetric or titrimetric); S reduction.

759. West, P. W., "Spot Test Procedures," in Comprehensive Analytical Chemistry, C. L. Wilson, Ed., Vol. IA, p. 387, Elsevier Publishing Company, Amsterdam (1959).

Spot test ($Hg[NO_3]_2$).

760. White, C. E., Fluorescene Analysis, p. 99, Marcel Dekker, Inc., New York, (1970).

Determination of $SO_4^=$ by excess thorium determination using morin.

SAMPLING

761. Adams, D. F., "Analysis of Sulfur Containing Gases in Ambient Air Using Selective Prefilter and a Micro Coulometric Detector," APCA, 18(3):145 (1968).

Sampling; not specific for $SO_4^=$.

762. Barton, S. C., "Preparation of Glass Fiber Filters for Sulfuric Acid Aerosol Collection," Environ. Sci. Technol., 4:769-770 (1970).

Extracted filters with H_2SO_4 prior to sampling.

763. Barton, S. C., "A Specific Method for the Automatic Determination of Ambient H_2SO_4 Aerosol," Proceedings of the 2nd International Clean Air Congress, pp. 379-382, Academic Press, New York (1970).

Extracted filters with isopropyl alcohol to selectively remove H_2SO_4.

764. Cadle, R. D., "Determination of the Composition of Air-Borne Particulate Material," Anal. Chem., 23:196-198 (1951).

Particulate collected by impaction on microscope slides covered with mineral oil film and treated with various reagents; $BaCl_2$ test for $SO_4^=$.

765. Colucci, J. M., "Polynuclear Aromatic Hydrocarbons and Other Pollutants in Los Angeles Air," Proc. Int. Clear Air Cong., 2nd., 1970, pp. 28-35 (1971).

Measured aromatics, CO, Pb, THC, V, NO_x, and $SO_4^=$ using classical methods.

766. Commins, B. T., "Determination of Particulate Acid in Town Air," Analyst, 88:364-367 (1963).

Sample collected on 4.25 cm Whatman No. 1 filters in Perspex holder; up to 30 liter/min and up to 6 hr.

767. Corn, M., "Particulate Sulfates in Pittsburg Air," APCA, 15(1):26-30 (1965).

Cascade Impactor sampling. $BaSO_4$ analysis.

768. Corn, M., "Sulfate Particulates - Size Distribution in Pittsburg Air," Science, 143(3608):803-804 (1964).

$SO_4^=$ may be better indicator of atmospheric pollution than SO_2.

769. Dubois, L., "Determination of Sulfate in Air," Int. J. Environ. Anal. Chem., 1(2):113-122 (1971).

Glass Fiber Filters may be source of error in $SO_4^=$ determination.

770. Forrest, J., "Ambient Air Monitoring for Sulfur Compounds. A Critical Review," J. Air Poll. Contr. Assoc., 23(9):761-768 (1973).

Review of sampling and analysis methods.

771. Gelman, C., "Estimation of Water-Soluble Chlorides, Sulfates, and Nitrates in Suspended Atmospheric Dusts," J. Air Poll. Contr. Assoc., 7(3):216-219 (1957).

Sampling on Whatman 41H filter paper; turbidimetric method for $SO_4^=$; advantage of cellulose filter paper.

772. Green, W. D., "Identification of Chemical Constituents in Single Aerosol Particles," Amer. Chem. Soc., Div. Water, Air Waste Chem., Reprints, 7(2):83-90 (1967).

Samples collected on glycerin-gelatin films containing a soluble Ba salt.

773. Hall, S. K., "Sulfur Compounds in the Atmosphere," Chemistry, 45(3): 16-18 (1972).

Discussion of health effects.

774. Higgins, F. B., Jr., "Sampling of Gases and Vapors," Source Samp. Atmos. Contam., Symp. Proc., 1971, pp. 47-62.

Review of sampling trains, procedures, and analytical methods.

775. Huey, N. A., "Determination of Sulfate in Atmospheric Suspended Particulates; Turbidimetric Barium Sulfate Method," U.S. Public Health Service Publ., 999-AP-11, I-1-I-4 (1965).

High volume collection on glass fiber. Water extraction-$BaSO_4$ method.

776. Jacobs, B., "Air Pollution and Atmospheric Analysis," Encycl. Ind. Chem. Anal., 1:99-121 (1966).

Review of sampling and analysis of air contaminants.

777. Junge, C. E., "The Concentration of Chloride, Sodium, Potassium, Calcium, and Sulfate in Rain Water Over the United States," J. of Meterology, 15(5):417-425 (1958).

A geographic survey.

778. Kiyoura, R., "Review of Direct Measurement Method of Sulfuric Acid Mist in Atmosphere," Preprint, Japan Chemical Society, Paper 3406, Jap. Chem. Soc. Ann. Mtg., 24th, Tokyo (1971).

Discussion of sampling techniques.

779. Leaky, D., "The Separation and Characterization of Sulfate Aerosol," Atmos. Environ., 9:219-229 (1975).

Studies pyrolytic and selective extraction for separation of sulfates. Also investigated filters.

780. Lee, R. E., "A Sampling Anomaly in the Determination of Atmospheric Sulfate Concentrations," Amer. Indus. Hyg. Assoc., J., 27:266-271 (1966).

SO_2 oxidized to $SO_4^=$ on filter elevates $SO_4^=$ readings for short term samples; solution to problem given.

781. Ludlam, F. H., "Atmospheric Aerosol," Sci. Progr., 42(165):65-75 (1954).

Sample deposited on slides behind two slits that divided > 0.9 μ and 0.1 to 0.9 μ particle radius.

782. Maddalone, R. F., "Radiochemical Evaluation of the Separation of Sulphuric Acid Aerosol by Micro-Diffusion from Various Filter Media," Mikrochim. Acta., 3:391-402 (1974).

Dubois work explained; glass-fibre poor, PTFE or graphite filters good.

783. Matsumura, Y., "Evaluation of Chemical Analysis Method of Sulfuric Acid Mist for Air Pollution," Rodo Eisei Kenkyusho Nenpo, pp. 48-49 (1971).

Discussion of analysis and sampling equipment and procedures.

784. Miller, J. M., "Rate of Sulfate Formation in Water Droplets in the Atmosphere with Different Partial Pressures of Sulfur Dioxide," Proc. Int. Clean Air Cong., 2nd, 1970, pp. 375-378 (1971).

Theoretical calculation of reaction rates.

785. Nakaoka, A., "Preparation of Standard Gas Containing Sulfuric Acid Aerosol. (Determination of Microamounts of Sulfur Trioxide in Atmosphere, Part I)," Tokyo Chuo Kenyusho Gijutsu Daiichi Kenkyusho Hokoku, (71044):1-19 (1971).

Discussion of filters and collection.

786. Nucciotti, F., "Improvements in Sampling Techniques and in the Methods for Determining Acid Gases in the Atmosphere," Riv. Ing., (5):353-356 (1969).

General sampling and analysis.

787. Quitmann, E., "Chemical Analysis of Mist Nuclei in the Atmosphere," Z. anal. Chem., 116:81-91 (1939).

Nuclei of moisture with radii of 10^{-8} to 10^{-4} cm condensed on chilled surface and examined ($SO_4^=$included).

788. Rauh, W., "Die Bestimmung von Freier Schwefelsäure in der Atmosphärischen Luft," *Z. gesammte Hygiene Ihre Grenzgebiete*, **18**:8-12 (1972).

Collected by impingement on copper foil.

789. Richards, L. W., "A New Technique to Measure Sulfuric Acid in the Atmosphere," Abstracts, 165th Natl. Meeting of the Amer. Chem. Soc., Dallas, Texas, April 1973, No. WaTR047.

Instrument: collects on filter, volatizes and measures with FPD.

790. Roesler, J., "Size Distribution of Sulfate Aerosols in the Ambient Air," *APCA*, **15**(12):576-579 (1965).

Sampling with Anderson Impactor.

791. Scaringelli, F. P., "Dynamic Calibration of an Acid Aerosol Analyzer," *JAPCA*, **16**(6):310 (1966).

792. Scaringelli, F. P., "Determination of Atmospheric Concentration of Sulfuric Acid Aerosol by Spectrophotometry, Coulometry, and Flame Photometry," *Anal. Chem.*, **41**(6):707-713 (1969).

H_2SO_4 separated from SO_2 and other sulphates. SO_3 in N_2 converted to SO_2 with hot Cu. SO_2 determined by FPD. Method can measure H_2SO_4 in presence of 100 times as much SO_2 and other sulphates.

793. Wagman, J., "Influence of Some Atmospheric Variables on the Concentration and Particle Size Distribution of Sulfate in Urban Air," *Atmos. Environ.*, **1**:479-489 (1967).

Discussion.

794. West, P. W., "Evaluation of Sulfur and Selenium Compounds as Air Pollutants," *Proc., Int. Symp. on Ident. and Meas. of Environ. Pollutants*, Ottawa, Ontario, Canada, 14-17 June 1971, pp. 38-43.(1971).

Discussion.

ADDENDUM

The following references were located after the report was submitted for approval.

795. Brosset, C., "Particle-Borne Acid: Occurrence, Effects and Determination Methods," Presented Before the Division of Water, Air and Waste Chemistry, Amer. Chem. Soc., August 1972.

796. Grennfelt, P., "Determination of Filter-Collected Airborne Matter by X-Ray Fluorescence, *Atmos. Environ.*, **5**:1-6 (1971).

797. Huygen, C., "A Simple Photometric Determination of Sulphuric Acid Aerosol," *Atmos. Environ.*, **9**:315-319 (1975).

Reacted with diethylamine and determined excess DEA photometrically.

798. Lukin, A. M., "Spectrophotometric Determination of Microamounts of Sulfates Using Chlorophosphonazo III," *Zavod. Lab.*, **40**(1):22-23 (1974).

Ba complex of chlorophosphonazo III reacted with $SO_4^=$ to release complexant. Decrease in absorbance of complex measured at 645 nm at pH 2.

799. West, P. W., "The Determination of Sulfuric Acid Aerosols," *Analyt. Chim. Octa.*, **69**:111-116 (1974).

Ring oven method. Not specific.

800. Zenki, M., "Titrimetric Method for Sulfate with Bisazochromotropic Acid Analogs as the Indicator," *Bunseki Kagaku*, **22**(8):1013-1017 (1973).

Titrate with Ba $(ClO_4)_2$ at pH 3. Sulfonazo III one of the best studied. A number of cations and anions interfere.